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**PROCEEDINGS:
SYMPOSIUM ON FLUE GAS DESULFURIZATION
NEW ORLEANS, MARCH 1976
Volume II**



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PROCEEDINGS:
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Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
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PREFACE

More than half of all "man-made" sulfur dioxide (SO_2) is emitted by electric power plants, and the use of sulfur-containing fossil fuels to generate electricity is predicted to increase by 50 percent by 1985. As a result, the development of SO_2 control technologies is one of the most important goals of the U.S. Environmental Protection Agency (EPA). Flue gas desulfurization (FGD) is the most promising technique for control of SO_2 that will be available for widespread application to fossil fuel-fired electric power plants for at least the next decade.

The Industrial Environmental Research Laboratory - Research Triangle Park (IERL-RTP) of EPA's Office of Research and Development sponsors symposia for the transfer of information regarding FGD research, development and application activities with the objective of further accelerating the development and commercialization of this technology. These symposia provide an opportunity for users and developers to discuss their experiences and the status of development and application of FGD technology.

The March 1976 symposium addressed full-scale FGD process applications in the U.S. and Japan as well as laboratory, pilot,

and prototype research and development efforts. The symposium also provided an opportunity for the announcement of data and results which were previously unreported or not widely publicized. The economics of FGD and the disposal, utilization, and marketing of FGD system by-products were also discussed. The symposium papers were presented by a cross-section of those concerned with FGD including users, government and private developers, and vendors. The electric utility industry--the principal user of FGD--participated extensively in the symposium program. More than 650 people attended the symposium.

These Proceedings are comprised of copies of the participating authors' papers as received. As supplies permit, copies of the Proceedings are available free of charge and may be obtained by contacting IERL-RTP's Technical Information Coordinator, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

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BY-PRODUCT DISPOSAL/UTILIZATION SESSION

Chairman: H. William Elder
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STATUS AND PLANS FOR WASTE DISPOSAL FROM UTILITY APPLICATIONS
OF FLUE GAS DESULFURIZATION SYSTEMS

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ABSTRACT

Approximately 10,000 MW of electricity generating capacity will be equipped with calcium-based scrubbing systems when those under construction are completed. Disposal of the waste solids produced will present formidable problems. The alternative disposal practices (storage in unlined ponds, use of liners, and fixation) in use or planned are discussed. Also, research in the utility industry on methods for disposal or utilization is summarized. Stringent requirements for final storage will make recovery processes (those that produce salable products) more competitive with the throwaway processes.

STATUS AND PLANS FOR WASTE DISPOSAL FROM UTILITY APPLICATIONS
OF FLUE GAS DESULFURIZATION SYSTEMS

INTRODUCTION

One might assume that a process that depends on solid and liquid phase concentration and composition, settled density, filterability, addition of secret ingredients, aging, and use of specially designed containers would result in a product that would be dispensed from a square bottle with a black label. Unfortunately, the product that is the subject for discussion is not nearly so popular but does affect those dealing with it in a variety of ways. The topic of course is sludge or as the Germans say in a more descriptive way, schlum.

The most recent count of systems operating or under construction shows that approximately 11,000 MW of generating capacity have or will have a flue gas desulfurization (FGD) system. Approximately 10,000 MW of the total are based on processes that produce calcium-based waste products. The result is that the utility industry is faced with an enormous solids waste handling and disposal problem. Utilities, government agencies, and research organizations have begun a sizable effort to identify and solve the problems associated with disposal or utilization of sludge. Much of this effort is described in subsequent papers. However, a summary of the current practice and plans for utility use of the technology should help to illustrate the variety of approaches presently being tried by those who have had to make decisions in the absence of clear guidelines.

The intent of this paper is to not only provide a compilation of the utility experience but to also encourage communication between the researchers and the users so that a more consolidated effort can be established.

CURRENT PRACTICE AND PLANS--FULL-SCALE INSTALLATION

The earliest installation of FGD systems generally incorporated the simplest and least expensive method of disposal, discharge to an unlined pond. Because of concerns about possible (but unestablished) effects of leaching on ground water quality, lined ponds have been provided at some installations. Most recently, chemical fixation of sludge has been chosen for some installations because of the improved structural properties of the waste solid and the increased resistance to leaching.

Unlined Ponds

A brief description of facilities with unlined ponds include the following:

Kansas Power and Light Company - Lawrence No. 4 and 5

Operation of the FGD system on unit 4 (125 MW) began in December 1968 and unit 5 (400 MW) started up in November 1971. Both units are equipped to burn gas when it is available and therefore sludge production has not been continuous. Waste solids, primarily a mixture of flyash and calcium sulfite, are discharged from both systems into a series of ponds with a combined surface area of 52 acres; the depth is unreported. Clarified liquor from the pond is recycled to the scrubbers and cooling tower blowdown is used for makeup. Good settling has been reported and the settled solids apparently solidify to some extent. No ground water degradation has been reported for this installation or for those listed below.

Kansas City Power and Light Company - Hawthorne No. 3 and 4

Operation of the scrubbing systems for these two units, 140 MW and 100 MW, respectively, began in 1972. The availability has been low and therefore the amount of solids discharged has also been low relative to the generating capacity.

The scrubber effluent, including flyash, is discharged to a clarifier; the overflow is recycled and the underflow from both systems is pumped to a 160-acre pond. The pond also is used for ash disposal from other units not equipped with scrubbers. Clarified liquor from the pond is not returned to the scrubbing systems.

Kansas City Power and Light Company - La Cygne No. 1

This new 820-MW unit began operation, along with its FGD system in mid 1973. Early availability was low, but recent operating time has improved at reduced load. Both flyash and SO_2 are removed in the absorbers and sludge is pumped to a settling pond with a capacity to accommodate about 5 yr of operation. Supernatant liquor is returned to the scrubbing system. Adequate settling has been obtained and the returned liquor is clear. Plans for disposal beyond the initial 5 yr have not been finalized.

Louisville Gas and Electric Company - Paddy's Run No. 6

The scrubbing system on this relatively small (70 MW) unit began operation in April 1973. The system has been used intermittently and for short periods. Flyash is removed ahead of the absorber. The sludge, almost entirely calcium sulfite, is collected in a clarifier where a flocculent is used to improve settling. Initially, the thickener underflow was dewatered on drum filters and trucked to a nearby borrow pit. Recently, the underflow (about 23% solids) has been treated with lime at the rate

of about 80 lb/ton of dry solids to stabilize the sludge. The treated waste solids are trucked to a landfill dump. Future sludge disposal studies to be conducted by Louisville Gas and Electric and sponsored by EPA are reported in another paper. Methods for disposal of waste solids from other planned Louisville Gas and Electric FGD systems have not been disclosed except for general planning.

City of Key West - Stock Island Unit

Operation of this small (37 MW) oil-fired unit and its scrubbing system began in the spring of 1973. The system is presently shut down, but during the period of operation, the waste solids containing a relatively large proportion of limestone (coral) were settled in a storage pond and the clarified seawater was discharged to the sea.

Arizona Public Service Company - Cholla No. 1

This 115-MW limestone scrubbing system was started up in late 1973. On-stream time has been high. Sludge disposal consists of pumping a sidestream from the scrubber directly to a settling pond. The same transport system and pond are used for ash disposal. No pond water is recycled to the scrubber system.

Nevada Power Company - Reid Gardner No. 1 and 2

These two 125-MW units were equipped with sodium scrubbing systems and began operation in 1974. They are listed here because they are operated as throwaway systems. The scrubber effluent from both units is pumped to a two-stage pond. The solids are settled out in the first pond and the overflow goes to a larger 45-acre evaporation pond. No liquor is recycled.

Public Service Company of Colorado - Valmont No. 5

The gas cleaning system on this unit treats a portion of the gas equivalent to 100 MW and was installed initially for particulate collection. In early 1975, addition of limestone was begun. Because of low inlet SO₂ concentration, the relative oxidation level is high and the sludge is composed mainly of calcium sulfate and fly ash. Solids separation takes place in a settling pond. Particle size segregation has been noted in the settled solids; near the point of discharge, the solids content is about 80% while sludge near the clarified liquor outfall contained only 40% solids.

Montana Power Company - Colstrip No. 1

Operation of the new 360-MW unit, equipped with lime scrubbing began in late 1975. The alkalinity from the flyash is utilized for SO_2 removal while the addition of supplemental lime is used for pH control in the scrubber (a developing trend, when feasible, for low-sulfur Western coals). Much like Valmont No. 5, the low inlet SO_2 concentration yields high relative oxidation and results in a sludge composed mainly of calcium sulfate.

Montana Power has chosen ponding as a method of disposal. They had first wanted to place the sludge back into the mine but the state would not permit this method of disposal.

The following approach is used. The flyash-calcium-sulfur product mixture is sluiced to a 15-acre temporary holding pond (operated on a closed-loop basis) which will be reclaimed by dredging. The resulting dredged slurry will be piped (15% solids) to an ultimate disposal site approximately 3 miles from the holding area. Excess water will be returned to the holding pond forming a closed-loop between the temporary and ultimate disposal area.

Monitoring wells are to be constructed around the pond site. After the disposal sites are filled, they will be covered and reclaimed.

Detroit Edison Company - St. Clair No. 6

A limestone scrubbing system on this 170-MW unit began operation in late 1975. Most of Detroit Edison's study of sludge disposal is a result of limestone scrubbing pilot-plant testing at the 1-MW level. The sludge produced in the Detroit Edison pilot plant was unique in that even though the flue gas had a high SO_2 content, the resulting sludge was high in calcium sulfate (approximately 90% CaSO_4). The normal sulfate content for their sludge should have been about 10-20%. The reason for this high degree of oxidation is still not clear.

Detroit Edison in conjunction with Marston Associates have studied a process that would pelletize sludge by utilizing the "plaster of paris" reaction. The process as tested required the conversion of some of the gypsum in the sludge into calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), which in turn was used in a drum granulator for pellet conversion. The end product was being viewed as a disposal product. Future status of this process is not clear.

At Detroit Edison's St. Clair Station, a 12-acre sludge disposal pond will be used to take care of 2 yr of sludge produced from the full-scale scrubber. The unit after 2 yr is scheduled to be converted over to low-sulfur fuel with the scrubber being used only for flyash control.

Kentucky Utilities Company - Green River No. 1, 2, and 3

The flue gas from three small (22 MW) boilers is treated in a lime scrubbing system; operation began in late 1975. The sludge contains a relatively large amount of calcium sulfate (40% oxidation) for a high-sulfur coal and a small quantity of ash. Solids are removed from the system in a diked settling pond with a storage capacity of about 5 yr. Clarified liquor is returned to the scrubber. During the short period of operation to date, settling has been good.

In addition to this listing of operating systems, 16 installations based on lime or limestone scrubbing are under construction. The method of disposal has not been published for many of these, but the number of those using unlined ponds for disposal of untreated sludge is likely to grow.

Lined Ponds

Information is available for only one installation in the United States that will utilize a lined pond, and it is not yet in operation.

Northern States Power Company - Sherburne No. 1 and 2

Two new 620-MW generating units are being equipped with limestone scrubbing systems; startup is planned in mid-1976 for the first unit and about a year later for the second. Low-sulfur Western coal will be burned and ash will be collected in the scrubbing system. Sludge (clarifier underflow) disposal will be in a 65-acre pond with 40-ft dikes and lined with 18 in. of clay. Clarified liquor will be returned to the scrubbing system. The pond is designed for a 10-yr life and additional capacity of similar construction will be added as needed for these two units. Future expansion at Sherburne County will be a problem because no additional pond space is available. To make matters worse, it will be difficult to find enough clay to line any additional ponds.

Tennessee Valley Authority - Widows Creek No. 8

A limestone scrubbing system is being installed on a 550-MW unit and operation will begin in early 1977. The pond is not actually lined, but has been constructed from local clay that would be suitable for use as a liner; the compacted material will result in low permeability. The 100-acre pond with 30-ft dikes is designed with a divider dike to permit maximum liquor retention time. Scrubber effluent with about 15% solids will be pumped to the pond and clarified liquor will be recycled. The estimated life of the pond is 7 yr. Additional capacity will be installed later.

Northwest German Power Company - Wilhelmshafen

Although this obviously is not a U.S. installation, the situation is interesting. A new 740-MW coal-fired unit will be completed in mid-1976. Gas volume equivalent to 145 MW will be treated with the Bischoff lime scrubbing process. This process was developed in a 35-MW prototype near Lunen where sludge storage leaching tests indicated that ground water quality was not affected. A clay-lined pond is being constructed and it will be operated with closed-liquor loop. However, the government has not yet approved a permit for its use.

Sludge Fixation

A sizable amount of development work by vendors and utilities has gone into methods for stabilizing sludge. The situation regarding use of this technology is as follows:

Commonwealth Edison Company - Will County No. 1

At Will County flue gas from a 167-MW cyclone boiler is cleaned by limestone scrubbers which in turn produce 200-250 tons of dry solids under full-load conditions. These solids are typical of this method of scrubbing in that they are composed of unreacted limestone, calcium sulfite, calcium sulfate, and flyash. After the scrubber, the sludge is pumped from the power station to a clarifier where the solids content is increased from 8 to 12% to approximately 35% solids. After dewatering, the sludge is mixed with additives for fixation purposes.

Two fixation recipes have been used over the past few years. One consisted of adding 100 lb of portland cement and 400 lb of flyash per 2000 lb of dry sludge. The other consisted of adding 200 lb of lime and 400 lb of fly ash per ton of dry sludge solids. Initially, the sludge stabilization mixture was transported by mix trucks to a settling pond at the plant where it was allowed to fix. At present, the latter fixation recipe is used and the mixture is transported by redi-mix trucks to an offsite disposal area (under EPA permit) owned by the transporting contractor. The fixed sludge becomes strong enough to support construction machinery and trucks after minimal compaction.

The original ponded material has been removed from the initial settling pond. This material had fixed sufficiently to allow handling with front end loaders for loading into dump trucks.

Future disposal will consist of hauling part of the fixed sludge to a nearby site which is being developed as a golf course. An EPA disposal permit was also obtained for this disposal site.

The cost of this process is quoted at \$18.50/dry ton of sludge solids. The cost includes labor, flyash, cement or lime handling, redi-mix trucks, front end loaders, and maintenance. It is reported that this operating cost could be reduced by \$4 to \$5/ton of dry solids if a pugmill were used.

Duquesne Light Company - Phillips Station

Duquesne Light has been using the Dravo stabilizing agent, Calcilox, since early 1974 to fixate sludge produced by the lime flue gas desulfurization system located at their 410-MW Phillips Station.

The sludge is first dewatered in a clarifier to about 35-40% solids. The clarifier underflow is then mixed with 200 lb Calcilox per dry ton of solids and sent to one of three 6,500 yd³ ponds for curing which requires approximately 30 days. The purpose of having three ponds is to have one for receiving, one for curing, and the last for excavating. Excavation is required to remove the fixed sludge from the pond for transportation to the final disposal site where it is mixed and compacted with dry flyash from the precipitator. The station's ash disposal area, located about a mile from the plant, is used for this purpose. Areas that become filled are covered with top soil and seeded.

Based on the capacity of the present disposal site, it will be completely filled in 2 yr. To solve this problem, Duquesne has requested proposals from Dravo, IU Conversion Systems, and U.S. Utilities Service Corporation, a company currently involved with the present ash removal and sludge treating activities. No firm proposals had been received as of November 1975, although U.S. Utilities has indicated it will propose a method of handling both the flyash and the sludge.

IU Conversion Systems has an 18-mo contract with Duquesne to handle the sludge produced by a 200-MW lime scrubber located at Duquesne Light's Elrama Station. The equipment used to make synthetic aggregate at Southern California Edison's Mohave Station has been brought in for the test periods.

Southern California Edison Company - Mohave Station

Much of the SCE full-scale sludge-disposal-related research was carried out at the Mohave scrubber installation. The sludge produced here was similar to other sludges which are a product of scrubbing flue gas with a low SO₂ inlet concentration; it was composed mainly of calcium sulfate. Therefore the Mohave sludge dewatered well (60-70% solids) and was fairly stable without further treatment.

Primary treatment of this sludge consisted of dewatering in a thickener where both cationic and anionic flocculents were added, one for the flyash fraction, the other for the sulfur products. After settling, the underflow was subjected to fixation procedures. SCE was under contract with both Dravo and IU Conversion Systems to perform fixation studies.

The Dravo process took the thickener underflow, added Calcilox, and sometimes lime, and placed the mixture in a pond for hardening; some hydrogen sulfide odor was detected in the vicinity of this pond.

The IUCS work led to the production of a synthetic aggregate. Most of the work was carried out in secrecy (tests conducted at an isolated area surrounded by a fence) and details of the process are not available. It was learned that control of the production step presented problems in that the recipe for producing a good quality aggregate was critical. Under certain conditions, the aggregate was fine and was easily blown away, while with only a small change in process variables, the product became very sticky. The process was however optimized and a paved parking lot demonstration test using this aggregate was made in Las Vegas.

SCE will probably not use a fixation process at Mohave for sludge disposal since calcium sulfate is somewhat stable and enough land area exists at the Mohave site to take all the sludge produced for the life of the plant (estimated to require 4,000 acre-ft).

Ohio Edison Company - Bruce Mansfield No. 1 and 2

Two new 880-MW units are being equipped with lime scrubbing systems; one unit recently started up but the disposal system is not fully operational. Dravo has the contract for waste disposal. Clarifier underflow containing about 30% solids will be mixed with Calcilox and pumped to the disposal area approximately 7 miles from the power station. The site consists of a large landfill ravine behind a 450-ft dam constructed for the project. The estimated life of the disposal area is 30 yr. Clarified liquor will be pumped back to the scrubbing system.

Other Installations

Other planned installations of fixation processes include:

<u>Installation</u>	<u>Startup date</u>
Louisville Gas and Electric Cane Run No. 4, 178 MW	June 1976
Louisville Gas and Electric Mill Creek No. 3, 425 MW	June 1977
Columbus and Southern Ohio Electric Conesville No. 5 and 6, 400 MW each	1976 and 1978
Indianapolis Power and Light Petersburg No. 3, 530 MW	1977

RESEARCH AND DEVELOPMENT BY UTILITIES

In addition to application of disposal technology to operating or planned flue gas desulfurization systems, several utilities are conducting experimental work on different methods for handling the waste problem. The following listing is not intended to be all-inclusive. Many utilities have conducted pilot-plant studies, mainly in conjunction with vendors, and several have also investigated stabilization.

Tennessee Valley Authority

Over the past several years, TVA has been involved extensively in sludge disposal studies, both for its own program and in support of the EPA program. Operation of a 1-MW limestone pilot plant to provide design information for the full-scale Widows Creek unit provided an opportunity to become intimately familiar with waste solids. This experience has been reported in previous symposia in this series. A major portion of the EPA scrubber sludge disposal program is being carried out at the TVA Shawnee plant and is reported in another paper.

Additional studies are under way as part of the research effort funded by energy-related pass-through funds from EPA to TVA. The main elements of this program include:

1. A technical, economic, and environmental impact evaluation for the production of granular fertilizer from scrubber product sludge.
2. A study to determine the range of variability of the solids from the scrubbers operated at the Shawnee test facility and a correlation of this variability with plant and scrubber operating conditions.
3. An economic-engineering evaluation of alternative sludge disposal methods.

TVA is also under contract with EPRI to provide solids characterization and scrubber correlation at several full-scale scrubber installations now in operation in the utility industry.

Southern California Edison

SCE is operating a 10-MW lime scrubber at its Highgrove plant. The main purpose is to evaluate their horizontal scrubber efficiency when using high-sulfur fuel oil. Because of the high SO_2 content in the flue gas, the oxidized sulfur constitutes a small percentage of the total sulfur absorbed (200 ppm out of 2,000 oxidized); thus the sludge is composed mainly of calcium sulfite (90% CaSO_3), the opposite of what was seen at Mohave. Edison has tested and developed a process to oxidize the calcium sulfite to calcium sulfate that yields 97% oxidation with air oxidation and pH control.

SCE hopes to develop a market for the oxidized sludge in the wallboard industry and will probably make a 50-ton full-scale wallboard test with Kaiser Cement Company.

Another interest of SCE is a method of sludge utilization where the oxidized sludge is used in agriculture. Gypsum promotes growth of denitrifying bacteria in soils containing high concentration of nitrates. It has also been found to promote the growth of alfalfa and peanuts and is a useful additive on any sulfur-deficient soil.

Other testing has included dewatering studies using thickeners, filters, and centrifuges and drying studies using spray dryers, thermal disc dryers, and kiln dryers. Some study of pelletizing has also been made.

SCE is also studying the feasibility of mixing scrubber sludge with ash from the coal-fired Kaiparowits Generator Station as a lining for reservoirs and for a structural fill or road subbase.

Southern Services

As a result of testing three flue gas desulfurization processes at Plant Scholz (20 MW each), Southern Services has become involved in both disposal and utilization studies on waste products from the Chiyoda gypsum process and the CEA-ADC dual alkali process.

Southern Services has contracted with both National Gypsum and United States Gypsum for bench-scale testing to determine the suitability for using Chiyoda gypsum in wallboard plants. Southern Services is also interested in the agricultural applications of using this gypsum, especially in the area of peanut farming.

At Plant Scholz the sludges are being ponded in two ponds which are equipped with underdrains so as to collect leachate samples for subsequent analyses of both major constituents and trace elements.

Fixation work is also being conducted on the dual alkali sludge. Flyash, portland cement, and quicklime are being added to the sludge in various concentrations and combinations so as to define the more promising fixation scheme. IUCS and Amax have also had an opportunity to test their processes on the sludge material.

Southern Services also plans to conduct economic and engineering evaluations for large-scale sludge-handling systems, such as pumping, conveyors, etc. Plans have been made for prototype and demonstration testing of the phases of study that prove to be promising.

Ontario Hydro

Ontario Hydro has been involved in the study of flue gas desulfurization systems for several years and has looked at almost every aspect of dealing with the resulting sludge disposal problem. Research at Hydro has been broad and in some of the major areas of concern, quite intensive. Test work has covered sludge dewatering techniques such as thickeners, vacuum filters, centrifuges and various combinations of each. Various fixation schemes using flyash, quicklime, and portland cement have also been evaluated, including defining their effect on permeabilities and strength. Advanced studies have included bench-scale work dealing with the regeneration of the product sludges to produce a salable sulfur product and lime or limestone for reuse.

In the area of sludge dewatering, this progressive utility has studied the effect of polyelectrolytes on settling, the mechanics involved during the thickening, and methods of improving the efficiencies of the thickener. At the pilot scale, they have evaluated the thickener-vacuum filtration scheme and a solid bowl continuous centrifuge to determine efficiencies and for comparison purposes.

The regeneration studies have centered on reductive roasting of lime or limestone product sludges to form calcium sulfide with subsequent carbonation of the aqueous slurry of calcium sulfide to recover calcium carbonate and to produce hydrogen sulfide for sulfur recovery. As a result of this testing, much has been learned about the thermodynamics and kinetics of the main reaction. Based on these results, Hydro has prepared preliminary flowsheets and material and energy balances for the regeneration reactions. Estimates of the capital and operating costs have also been made.

Southwestern Public Service Company

Southwestern Public Service Company in conjunction with Combustion Engineering is also involved in studying the feasibility of producing structural landfill material from sludge by mixing scrubber solids with local soils found around the plant site. Their tests demonstrated that mixtures of soil and sludge could produce a landfill material with significant load-bearing strength. This type or method of approach looks more promising in areas that have a more arid climate.

Empire State Electric Energy Research Corporation (ESEERCO)

A possibility exists that ESEERCO and the State of New York (Office of Environmental Planning) may become involved in a joint program whereby the feasibility of using sludge stabilized by the IUCS process for the construction of fish reefs off the coast of Long Island will be studied. No decision for this program has been made.

CONCLUSIONS

The only firm conclusion that can be drawn with the current situation is that this paper has come to an end--yet the story has just begun. A few subjective generalizations probably won't do any harm.

Disposal of untreated sludge in unlined ponds has been in progress for up to 8 yr with no apparent adverse effect on surface or ground water quality. However, the extent of evaluation of effects is unclear. Obviously, this is the least cost approach to disposal provided that storage areas are available. Major unquantified factors with this method are: (1) potential hazard from the quicksand nature of many sludges, (2) commitment of land to nonproductive use, (3) potential long-term effects of leaching if and when attenuation capacity is exceeded, and (4) likelihood of solid waste regulations whether they are needed or not.

The problem with uncertain effects of leaching can be dealt with by providing, at some increased cost, a low permeability lining. The specifications for alternative materials regarding method of placement, chemical resistance, mechanical durability, and resistance to varmits of the above-ground and underground types need to be established before meaningful economic trade-offs can be considered.

Perhaps the land use problem can be handled best by conversion, at some increased cost, of calcium sulfite to calcium sulfate (gypsum) so that the waste solids can be used for landfill as long as convenient holes are available. Studies under way should provide some answers to questions (including the cost and whether there is a leaching problem) associated with this method.

EPA has made its position fairly clear that chemical fixation or stabilization is the preferred method. It will undoubtedly be the most expensive. With this approach, all of the risks are reduced substantially, but it would be good to know if it is worth the cost. Any good insurance man will tell you that you can be overinsured.

One advantage to fixation is that the added cost to throwaway processes will make recovery processes more competitive and likely the economic choice in many situations. The advantage is that sulfur would be recovered in a useful form and our natural reserves would be conserved. However, one can't help but be sympathetic with the poor fellow who would be stuck with the disposable variety.

RESEARCH AND DEVELOPMENT FOR CONTROL OF WASTE AND WATER
POLLUTION FROM FLUE GAS CLEANING SYSTEMS

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ABSTRACT

The EPA Program for Control of Waste and Water Pollution from Flue Gas Cleaning (FGC) Systems is designed to evaluate, develop, demonstrate and recommend environmentally acceptable, cost-effective techniques for disposal and utilization of FGC wastes, with emphasis on Flue Gas Desulfurization (FGD) sludge, and to evaluate and demonstrate systems for maximizing power plant water reuse/recycle. The program currently consists of nineteen projects, each covering one of six areas of interest--(1) environmental assessment of FGC waste disposal/utilization processes and other power plant effluents, (2) assessment of the technology of these processes and development of new technology, (3) studies of the economics of these processes, (4) development of alternative FGC waste disposal methods, (5) development of new FGC waste utilization methods, and (6) development of methods for improving overall power plant water use.

The environmental assessment efforts include FGC waste characterization studies; laboratory and pilot field studies of disposal techniques for chemically treated FGD sludges; characterization of coal pile drainage, coal ash, and other power plant effluents; and studies of attenuation of FGC waste leachate by soils. The technology assessment and development efforts include field studies of untreated and chemically treated FGC wastes; FGC waste leachate-disposal site liner compatibility studies; studies to correlate waste solid characteristics with scrubber operating conditions; and dewatering equipment design studies. Alternate disposal method studies include both mine and ocean disposal assessments. The economic studies include cost estimates of current disposal practices (e.g., ponding, landfill) and by-product marketing studies. Utilization efforts include development of a process for FGC waste conversion (to sulfur and calcium carbonate); pilot studies of fertilizer production (using the waste as a filler material and a source of sulfur); use of FGD gypsum in portland cement manufacture; and FGC waste beneficiation studies. The power plant water use effort is a single study to minimize water use and waste water discharges.

Results from this program can accelerate increasing use of domestic coal supplies in power plants.

This paper has been reviewed by the Environmental Protection Agency and approved for presentation. Mention of trade names, commercial products, or commercial processes does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

A major consideration inherent in plans for installing a flue gas cleaning (FGC) system is the necessity for disposing of or utilizing the by-products. This is true for all coal-fired boilers, especially those with flue gas desulfurization (FGD) systems. Application of FGD systems in the United States is accelerating; the majority of these are lime/limestone wet scrubbing systems which produce a calcium/sulfur by-product. Because of environmental and economic concerns related to the disposition of this FGD waste, there have been considerable governmental and industrial research, development, and demonstration activities. Modest EPA efforts in this area were begun in the late 1960's in support of the limestone scrubbing program. In late 1972, major research and development (R&D) efforts were initiated; these efforts were described by the author in a previous paper.¹ In late 1974, plans were formulated to greatly expand these R&D efforts as part of EPA's Energy Research Program. These efforts were aimed at determining pertinent environmental parameters, reducing costs, investigating alternative strategies, and encouraging by-product usage. Although the major emphasis in these new efforts was on FGD wastes, they involved consideration of overall power plant waste and water problems, including the disposal and utilization of coal ash. For this reason, the new program was entitled "Control of Waste and Water Pollution from Flue Gas Cleaning (FGC) Systems". In this paper, the program will be referred to as the FGC Waste and Water Program.

The FGC Waste and Water Program developed in Fiscal Year (FY) 1975 consisted of the expansion and/or extension of four existing projects and the addition of twelve new projects. In FY 1976, three new projects are being added, for a total of nineteen. Each of the projects is listed in Table 1; the contractor or agency performing the project is listed, along with funding by Fiscal Year.

2.0 PROGRAM PHILOSOPHY

The objectives of the FGC Waste and Water Program are to evaluate, develop, demonstrate and recommend environmentally acceptable, cost-effective

Table 1: Projects in FGC Waste and Water Program

Project Title	Contractor/Agency	Funding, \$1000				FY 77-80 (est.)	Totals
		Prior to FY 75	FY 75	FY 76			
FGC Waste Characterization, Disposal Evaluation, and Transfer of FGC Waste Disposal Technology	The Aerospace Corporation	596	500				
Lab and Field Evaluation of 1st and 2nd Generation FGC Waste Treatment Processes	U.S. Army Corps of Engineers Waterways Experiment Station	110	325				
Characterization of Effluents from Coal-Fired Power Plants (Waste and Water only) ^a	Tennessee Valley Authority	-	300				
Ash Characterization and Disposal	Tennessee Valley Authority	-	300				
Studies of Attenuation of FGC Waste Leachate by Soils	U.S. Army Materiel Command Dugway Proving Ground	75	300				
Establishment of Data Base for FGC Waste Disposal Standards Development	Stearns, Conrad and Schmidt Consulting Engineers, Inc. (SCS Engineers)	-	150				
Shawnee FGC Waste Disposal Field Evaluation	Tennessee Valley Authority/The Aerospace Corporation	(203) ^b	(250) ^b				
Louisville Gas and Electric Evaluation of FGC Waste Disposal Options	Louisville Gas and Electric Company (Subcontractor: Combustion Engineering)	-	750				
FGC Waste Leachate-Liner Compatibility Studies	U.S. Army Corps of Engineers Waterways Experiment Station	-	100				
Lime/Limestone Wet Scrubbing Waste Characterization	Tennessee Valley Authority	-	40				
Dewatering Principles and Equipment Design Studies	Auburn University	-	-				
Conceptual Design/Cost Study of Alternative Methods for Lime/Limestone Scrubbing Waste Disposal	Tennessee Valley Authority	-	100				
Gypsum By-Product Marketing Studies	Tennessee Valley Authority	-	100				
Evaluation of Alternative FGC Waste Disposal Sites	Arthur D. Little, Inc.	-	250				
Lime/Limestone Scrubbing Waste Conversion Pilot Studies	M. W. Kellogg Company	-	92.4				
Fertilizer Production Using Lime/Limestone Scrubbing Wastes	Tennessee Valley Authority	-	110				
Use of FGC Gypsum in Portland Cement Manufacture	Contractor Selection Pending	-	-				
FGC Waste/Fly Ash Beneficiation Studies	TNW, Inc.	-	-				
Assess/Demonstrate Power Plant Water Reuse/Recycle	Radian Corporation	-	200				
Totals		781	3617.4	2549	4685	11,632.4	

^a This project also includes gaseous emission characterization efforts; additional funds (not shown here) are provided for those efforts.^b Funds for this project included in Shawnee lime/limestone scrubbing project funds, therefore not included in program totals.

techniques for disposal and utilization of FGC wastes, with emphasis on FGD wastes, and to evaluate and demonstrate systems for maximizing power plant water reuse/recycle.

To accomplish these objectives, projects were undertaken covering a broad range of activities to thoroughly evaluate existing technology and explore new, not-yet-commercial concepts. Six areas of interest were identified as requiring attention; these areas reflect the basic philosophy behind the FGC Waste and Water Program. The areas of interest are:

- (1) Environmental assessment of FGC waste disposal/utilization processes and other power plant effluents
- (2) Assessment of the technology of these processes and development of new technology
- (3) Studies of the economics of these processes
- (4) Development of alternative FGC waste disposal methods
- (5) Development of new FGC waste utilization methods
- (6) Development of methods for improving overall power plant water use

Table 2 shows the relationship of each of the projects to the areas of interest listed above. It is readily apparent that only four of the projects are aimed at investigating one specific area; most of the projects cover several areas of interest. This is to be expected, since it would be difficult, for example, to assess the technology of a process without examining both the economics and the environmental effects. However, each of the projects does have, as its main function, a single area of interest. With this in mind, each of the projects in the FGC Waste and Water Program is described in the next section under the heading of the main area of interest addressed in the project.

3.0 FGC WASTE AND WATER PROJECTS

In this Section, each of the projects is briefly described, and the current status of the project is discussed. For readers interested in more detailed information, the EPA Project Officer and the Contractor or Agency Project Director are also indicated.

Table 2: Relationship of Projects to Areas of Interest
in FGC Waste and Waste Program

<u>Project</u>	<u>Areas of Interest</u>					
	<u>Environmental Assessment</u>	<u>Technology Assessment/Development</u>	<u>Economic Studies</u>	<u>Alternative Disposal Methods</u>	<u>Utilization Methods Development</u>	<u>Overall Power Plant Water Use Development</u>
FGC Waste Characterization, etc. (Aerospace)	X	X	X	X		
1st and 2nd Generation Waste Treatment Processes (Corps of Engineers)	X	X				
Characterization of Power Plant Effluents (TVA)	X					
Ash Characterization (TVA)	X	X	X			X
Leachate-Soil Attenuation (Army Materiel Command)	X					
Establishment of Data Base For Standards (SCS Engineers)	X	X				
Shawnee Field Evaluation (TVA/Aerospace)	X	X	X	X		
Louisville Waste Disposal Evaluation (LG&E/Combustion Engineering)	X	X		X		
Leachate-Liner Compatibility Studies (Corps of Engineers)		X	X			
Scrubber Waste Characterization (TVA)		X				
Dewatering Studies (Auburn University)		X				
Conceptual Design/Cost Studies for FGC Waste Disposal (TVA)		X	X			
Gypsum By-Product Marketing Studies (TVA)		X	X			
Evaluation of Alternative Disposal Methods (A.D. Little)	X	X	X	X		
Scrubbing Waste Conversion Studies (M.W. Kellogg)			X		X	
Scrubbing Waste in Fertilizer (TVA)			X		X	
Gypsum in Portland Cement (Not Selected)		X	X		X	
FGD Waste/Fly Ash Beneficiation (TRW)			X		X	
Assess/Demonstrate Power Plant Water Reuse/Recycle (Radian)			X			X

3.1 Environmental Assessment

3.1.1 FGC Waste Characterization, Disposal Evaluation, and Transfer of FGC Waste Disposal Technology -

This is a contract (68-02-1010) with Aerospace Corporation, under which a broad-based, on-going study is being performed to (1) identify environmental problems associated with FGC waste disposal by comparing chemical and physical characteristics of the waste with current, proposed, or potentially applicable environmental standards; (2) assess current FGC waste disposal methods, including feasibility, performance, and costs--by conducting laboratory studies of wastes as they would be disposed, providing engineering support and conducting chemical/physical analyses for the Shawnee field evaluation (see below), making an evaluation of other available field data, and conducting engineering cost studies of disposal methods; (3) make recommendations regarding alternate disposal approaches based on (1) and (2); and (4) assemble, assess, and report all FGC waste-related R&D activities in EPA, TVA, and private industry. This project is the key effort in the EPA FGC Waste and Water Program.

Formal reports on the Shawnee field evaluation are planned annually; integrated R&D reports of government and industry activities are planned annually; and technical papers will be presented approximately every 18 months at EPA FGD symposia. Initial results from this contract have been reported.^{1,2,3} Additional results of Aerospace laboratory studies will be released in a report within the next few months. The first annual integrated R&D report, to be released in the Spring of 1976, will summarize the results from all the projects described in this paper.

Currently, most of the efforts under this project, with the exception of the Shawnee field evaluation support and the R&D integration effort, are coming to a conclusion. The project has generated significant information, examples of which follow:

- (1) Chemical analysis of FGD waste liquors has revealed the need for protection of ground and surface waters because of excess (over drinking water standards) of chloride, sulfate, and several of the trace metals.¹

- (2) Physical characterization of FGD wastes has quantified the effect of moisture on physical properties; i.e., approximately 65-70 percent solids content is required for landfill operation.¹
- (3) Chemical fixation of FGD wastes can drastically reduce the rate of pollutant release to the environment by decreasing the solubility and permeability of the waste and by physically stabilizing the material so that it can be placed in a landfill.⁴
- (4) Costs of chemical fixation processes depend to a great extent on local plant conditions (e.g., land availability), but a reasonable total disposal cost appears to be in the range of \$9-10/metric ton (dry solids basis), or about 1.1-1.2 mills/Kwhr for a typical plant.⁴

The EPA Project Officer for this project is the author of this paper. The Aerospace Project Director is Jerry Rossoff.

3.1.2 Lab and Field Evaluation of 1st and 2nd Generation FGC Waste Treatment Processes -

This is an Interagency Agreement (EPA-IA-G-D4-0569) with the U.S. Army Corps of Engineers' Waterways Experiment Station (WES) under which laboratory and field studies are being conducted to evaluate current commercial (1st generation) and new, not-yet-commercial (2nd generation) processes for treatment (e.g., chemical fixation) of several industrial wastes, including FGC wastes. The 1st generation processes will be evaluated through laboratory leaching column studies, physical testing of samples of several FGC wastes treated by chemical fixation processors, and small field studies of selected fixation processes. Initial efforts in this project are similar to the Aerospace laboratory studies of chemical fixation processes, except that additional commercial processes are being evaluated. In addition, visits will be made to existing full-scale disposal sites for complete evaluation of current disposal practices, including coring of soil beneath disposal sites.

The 2nd generation processes will be identified through a literature survey and will be restricted to those which are chemically and operationally defined. Candidate processes will be screened via an economic analysis, laboratory physical testing, and laboratory testing to determine resistance to pollutant leaching. Based on the screening results, no more than five processes will be selected for comprehensive evaluation, consisting of studies similar to those conducted for the 1st generation processes.

An interim report on physical testing and leaching tests of the 1st generation processes is expected to be issued in April 1976. In addition, a paper summarizing this information is being presented at this symposium.⁵ For this reason, a status report on this project will not be given here. Final reports on the 1st and 2nd generation studies are expected in mid-1977 and mid-1978, respectively.

The EPA Project Officer for the WES efforts is Robert E. Landreth, a Sanitary Engineer with the Municipal Environmental Research Laboratory in Cincinnati, Ohio. The WES Project Director is Dr. Jerry L. Mahloch.

3.1.3 Characterization of Effluents from Coal-Fired Power Plants -

One of several tasks being conducted by the Tennessee Valley Authority (TVA) under an Interagency Agreement (EPA-IAG-D5-E-721), this project involves efforts to (1) characterize and quantify the chemical parameters of coal pile drainage, (2) assess and quantify the chemical and physical composition of ash pond effluent after adjustment of pH and suspended solids reduction to meet effluent standards, (3) evaluate an ash pond monitoring program to determine the sampling and analyses necessary to obtain representative information, (4) assess, characterize, and quantify the effects of coal ash leachate on ground water quality, and (5) evaluate and quantify the chlorinated effluent in the discharge canal from once-through cooling systems.* Information from this project will be supplemented by TVA fly ash

*This project also includes a major effort to characterize and quantify the gaseous and particulate emissions from at least three typical coal-fired boilers (including tangential and wall-fired) and at least one scrubber. Although the emission characterization effort is not considered part of the FGC waste and water program, the emission data will be combined with FGC waste data to attempt an overall emissions/effluent material balance.

characterization efforts (see below). Reports on each of these efforts will be issued as the specific effort is completed. The final report is planned to be released in late 1978.

The experimental design for the coal pile drainage study (which involves two TVA plants) has recently been completed; sampling and flow measurement equipment has been ordered. The coal pile drainage test program is expected to be underway soon. In the ash pond effluent study, a computer model has been developed to simulate the batch settling characteristics of fly ash and bottom ash in a continuous ash pond system. Preliminary ash pond field data indicate that cenospheres may be the major factor contributing to high suspended solids in the ash pond effluent and that pH adjustment may be somewhat more difficult than originally envisioned. In examining the effects of coal ash leachate, the experimental design for soil coring and ground water studies is complete and is expected to be underway soon. A plant has been selected for the chlorinated cooling system effluent study; i.e., to determine the minimum effective chlorine dosage to control biological fouling.

The EPA Project Officers for this project are Ronald A. Venezia and the author of this paper. The TVA Project Directors are Drs. Billy G. McKinney and Hollis B. Flora, II of TVA's Power Research Staff, Chattanooga, Tennessee.

3.1.4 Ash Characterization and Disposal -

One of several tasks being conducted by TVA under an Interagency Agreement (EPA-IAG-D5-E-721), this project involves efforts to (1) summarize and evaluate existing data on the characteristics of coal ash and ash effluents from in-house TVA studies and from studies made by other organizations; (2) perform chemical and physical analyses on coal, coal ashes, and ash effluents to obtain a complete characterization of these materials as a function of variation in boiler design and operation, as well as coal type; (3) evaluate various methods for disposal and utilization of fly ash; (4) summarize information on methods of ash sluice water treatment for reuse; (5) conduct conceptual design studies of dry and wet ash handling systems; and (6) recommend the most promising systems for ash handling and disposal/utilization. Reports on each of these efforts will be issued as the

specific effort is completed. The final report on the project is planned for January 1979.

The summary of available data on coal and ash characterization is essentially complete. The major experimental effort under this project, item (2) in the preceding paragraph, is being coordinated with the gaseous emission studies in the project described in 3.1.3, above, and is not expected to be in "high gear" until the late spring of 1976. However, a "dry run" to verify the rather complicated sampling and analytical program has already been successfully accomplished.

The EPA Project Officer for this project is the author of this paper. The TVA Project Director is Ms. Shirley S. Ray of TVA's Power Research Staff.

3.1.5 Studies of Attenuation of FGC Waste Leachate by Soils -

This is an Interagency Agreement (EPA-IAG-D4-0443) with the U.S. Army Materiel Command's Dugway Proving Ground under which a study is being conducted to determine the extent to which heavy metals and other chemical constituents in several industrial wastes, including FGC wastes, can migrate through the soil in land disposal sites. At least six scrubber wastes and three coal fly ashes will be tested under this project. The project will consist of the following efforts: (1) physical and chemical characterization of the wastes; (2) leachate studies in columns with the wastes applied to a variety of U.S. soil types; (3) long term permeability tests with selected clays; and (4) interpretation of data from the tests in (1) and (2) to identify soil attenuation mechanisms and to develop empirical "attenuation coefficients" for specific chemical substances. The final report for the project is expected to be issued in late 1977.

Characterization of three of the FGC wastes has been completed; permeability tests with these wastes are currently underway. The leachate columns have been designed; several have been fabricated. The leaching studies are expected to begin in March 1976. All of the scrubber wastes and soils should be under test by the end of April. A preliminary progress report on the leaching tests should be available by late 1976.

The EPA Project Officer for this project is Dr. Mike Roulier, a Research Soils Scientist with the Municipal Environmental Research Laboratory in Cincinnati, Ohio. The Dugway Project Director is Dr. Martin Houle.

3.1.6 Establishment of Data Base for FGC Waste Disposal Standards Development -

This is a contract (68-03-2352) with SCS Engineers which includes efforts to: (1) establish the criteria necessary to evaluate FGC waste disposal options; (2) compile any proposed or existing standards/regulations which have been or could be applied to the land disposal of FGC wastes; (3) evaluate the impact of applying existing and proposed standards/regulations; (4) determine the interrelationships between environmental effects and regulatory approaches, considering prevention of adverse health, ecological, and aesthetic effects; (5) develop a technical basis for future standards development; (6) recommend R&D to supply any additional information and/or technology needed to implement the standards. Initiated in November 1975, this effort is expected to be completed by late 1976; however, because of emerging technology in the area of FGC waste disposal, initial results are expected to require subsequent updating.

The EPA Project Officer for this project is Donald E. Sanning, a Research Chemist with the Municipal Environmental Research Laboratory in Cincinnati, Ohio. The SCS Project Director is C. J. Schmidt.

3.2 Technology Assessment and Development

3.2.1 Shawnee FGD Waste Disposal Field Evaluation -

This is part of an Interagency Agreement (EPA-IAG-D5-E-721) with TVA for lime/limestone scrubber tests at Shawnee. Under the current program, the Chemfix, Dravo, and IU Conversion Systems processes for chemical fixation of scrubber wastes are being evaluated in three separate disposal ponds. Untreated lime and limestone wastes are placed in two additional ponds. Leachate, run-off and ground water samples as well as core samples of the wastes and soil are being collected and analyzed to evaluate environmental effects. Both Aerospace Corporation and TVA are performing selected analyses; Aerospace is responsible for data evaluation and reporting. Future plans

call for evaluation of other disposal approaches, including gypsum disposal. Preliminary results from this effort are being reported by Aerospace in a separate paper at this symposium.⁶ For this reason, a status report will not be given here. The first formal report on this project is expected to be released later this month. The project is scheduled to be completed by September 1977.

The EPA Project Officer for this project is the author of this paper. The Aerospace Project Director is Jerry Rossoff; the TVA Project Director is James J. Schultz of TVA's Office of Agricultural and Chemical Development, Muscle Shoals, Alabama. The program is coordinated with the Shawnee scrubber test program directed by Bechtel Corporation for EPA.

3.2.2 Louisville Gas and Electric Evaluation of FGD Waste Disposal Options -

This is part of a contract (68-02-2143) with Louisville Gas and Electric Company (LG&E) to conduct a program of carbide and commercial lime scrubbing tests and an extensive evaluation of scrubber waste treatment/disposal options. Laboratory studies of non-chemical and chemical (fixation) processes for stabilization of scrubber sludge will be conducted using carbide lime and commercial lime scrubbing wastes; samples will be mixed with fly ash alone or fly ash and one of several additives (e.g., portland cement). Results of testing of the stabilized samples will be used to determine those mixtures to be field tested. The field studies will consist of (1) small-scale (about 19 cubic meter) impoundment tests in which leachate, run-off and physical stability tests of unstabilized and stabilized waste material will be conducted in above-ground "swimming pools", and (2) larger scale (about 76 cubic meter) landfill tests in which leachate migration, run-off, and physical stability tests of unstabilized and stabilized waste material will be conducted in landfill areas with in-situ clay and synthetic linings.

An interim report will be issued after completion of the laboratory (and part of the field) studies. The final report is expected to provide significant information on the technical and environmental acceptability of several scrubber waste disposal methods. The recently initiated project is expected to be completed by mid-1977; the interim report is expected to be issued in late 1976.

The EPA Project Officer for this project is the author of this paper. The LG&E Project Director is Robert P. Van Ness.

3.2.3 FGC Waste Leachate-Liner Compatibility Studies -

This is an Interagency Agreement (EPA-IAG-D5-0785) with the U.S. Army Corps of Engineers' Waterways Experiment Station (WES) under which a program is being conducted to (1) determine the compatibility of 18 liner materials with flue gas cleaning (FGC) wastes and associated liquors and leachates; (2) estimate the length of life for the liners, and (3) assess the economics involved with purchase and placement (including disposal area construction) of various liner materials. A review of the literature will be made to evaluate potential liner materials, including admixed materials (e.g., soil cements, asphalt cements, stabilized FGC waste), flexible materials (e.g., polyvinyl chloride, polyethylene), and sprayed-on materials (e.g., plastics, asphalts, sulfur). At least 18 materials will be selected for tests in exposure cells designed to simulate a depth of sludge/liquor of at least 6 meters. The liner materials will be subjected to physical tests to determine whether the exposure to the FGC wastes causes deterioration in the strength and/or permeability of the material; these will be conducted after zero (baseline testing), 12, and 24 months of exposure. The final report for this project is expected to be issued in the spring of 1978.

Ten chemicals that are admixed into soil, six chemicals that are sprayed onto soil, and two flexible materials that are placed over soil have been selected by WES for testing. The eighteen liner materials will be placed inside a 38 cm (15 in.) diameter test chamber which will be pressurized to simulate a 6 meter (20 ft) sludge/liquor head. The soil to be used in the admixes and base filler is a silty sand with a permeability of about 5×10^{-4} cm/sec. Baseline tests of the flexible materials are underway; optimum admixture compositions are currently being defined.

The EPA Project Officer for this project is Robert E. Landreth of the Municipal Environmental Research Laboratory in Cincinnati, Ohio. The WES Project Officer is Z. B. Fry.

3.2.4 Lime/Limestone Wet Scrubbing Waste Characterization -

One of several tasks being conducted by TVA under an Interagency Agreement (EPA-IAG-D5-0721), this project involves the physical and chemical characterization of lime/limestone wastes as a function of scrubber operating conditions. These studies are a continuation of efforts conducted during 1974 with Colbert pilot plant wastes. The Colbert waste solid crystals varied greatly depending on the presence of fly ash. Oxidation is another major factor affecting the crystal size and structure. Under these studies, TVA will (1) characterize waste materials from the Shawnee facility* and correlate the physical and chemical properties of the materials with the scrubber operating conditions (e.g., boiler excess air, liquor and gas flow rates, inlet and outlet scrubber liquor pH, and inlet SO_2 concentration), and (2) suggest, if feasible, a means of controlling waste characteristics, particularly the physical properties (such as ease of dewatering) to improve disposal or utilization economics. The initial Shawnee studies are expected to be completed by mid-1976; the final Shawnee studies should be completed by mid-1977.

So far, no distinct mathematical relationships have been shown between the properties of the waste solids and the scrubber system operational parameters. However, samples taken during high limestone utilization tests conducted in November 1975 at the Shawnee facility inferred the possibility of an inverse relationship between stoichiometric ratio and calcium sulfite hemihydrate crystal size. Greatly improved dewatering characteristics were evident at stoichiometric ratios near 1.0.⁷ Photomicrographs taken of samples from a test run at a stoichiometric ratio of 1.03 showed crystals several times larger than those from a test run at a stoichiometric ratio of 1.43. This relationship will be studied further.

*Under a separate study funded by the Electric Power Research Institute (EPRI), waste materials from other (full-scale) facilities will be obtained, and the physical/chemical properties will be correlated with scrubber operating conditions.

The EPA Project Officer for this project is the author of this paper. The TVA Project Director is James L. Crowe of TVA's Power Research Staff.

3.2.5 Dewatering Principles and Equipment Design Studies

This project, for which a grant application has recently been received from Auburn University, will consist of the following efforts to improve current FGC waste dewatering equipment: (1) an examination of current dewatering equipment design principles to determine their applicability to FGC wastes; (2) laboratory settling and other tests to determine the physical properties and behavior of FGC wastes as a basis for dewatering equipment design studies; (3) analytical design studies to develop dewatering equipment designs based on FGC waste physical properties and behavior (these efforts will continue and will be updated based on subsequent bench scale testing); and (4) laboratory tests of dewatering equipment design concepts. Further testing of the concepts developed may be conducted if there is sufficient interest expressed by private industry. This project offers the potential of cost savings through reduction in the size of dewatering equipment and the volume of the disposal site, as well as through reduction in the amount of chemical fixation additive (if used) required. The project is expected to be initiated in mid-1976 and should be completed by the fall of 1978.

The EPA Project Officer for this project is the author of this paper. The Auburn University Project Director is Professor James C. Warman.

3.3 Economic Studies

3.3.1 Conceptual Design/Cost Study of Alternative Methods for Lime/Lime-stone Scrubbing Waste Disposal -

This project is one of several tasks which make up the economic studies of major FGD processes being conducted by TVA under an Interagency Agreement (EPA-IAG-D5-E-721) (results of other economic studies have been reported in another paper at this symposium).⁸ In this project several FGD waste disposal methods and FGD system design and operating premises will be selected for a detailed economic evaluation of FGD waste disposal. Currently

available information, such as engineering cost estimates from the Aerospace contract and fixation vendor estimates from the Shawnee field evaluation, will be used in the initial efforts, with updating as additional information becomes available. Alternatives will very likely include variations in mechanical dewatering equipment, variations in treatment (e.g., oxidation to gypsum, chemical fixation), and variations in ultimate disposal (e.g., ponding, landfill). The final report on this two-year effort is expected in late 1977.

The EPA Project Officer for the TVA economic studies is Richard D. Stern of the Industrial Environmental Research Laboratory in Research Triangle Park, N. C. The TVA Project Director is H. Lewis Faucett of TVA's Office of Agricultural and Chemical Development, Muscle Shoals, Alabama.

3.3.2 Gypsum By-Product Marketing Studies -

This project is one of several tasks which make up the FGD by-product marketing studies being conducted by TVA under an Interagency Agreement (EPA-IAG-D5-E-721) (results of the sulfuric acid and sulfur marketing studies will be reported in another paper at this symposium).⁹ A preliminary study conducted by TVA during early 1974 indicated the possibility that production and sale of abatement gypsum might offer a substantial economic advantage over FGD waste disposal. These new studies include a thorough economic evaluation of gypsum producing processes (e.g., Chiyoda, carbon absorption, CaSO_3 oxidation) and a detailed U.S. marketing study of abatement gypsum for wallboard. A report on this study is expected in late 1976. Future plans include studies of abatement gypsum for use in portland cement manufacture.

The EPA Project Officer for the TVA marketing studies is Dr. Charles J. Chatlynne of the Industrial Environmental Research Laboratory in Research Triangle Park, N.C. The TVA Project Director is John I. Bucy of TVA's Office of Agricultural and Chemical Development, Muscle Shoals, Alabama.

3.4 Alternate Disposal Methods Development

This effort consists of a contract (68-03-2334) with Arthur D. Little, Inc. (ADL) under which a program is being conducted to identify, assess, and

demonstrate, on a pilot scale, alternate FGC waste disposal methods (other than local ponding and landfilling). The present program calls for the demonstration to be limited to coal mine and ocean disposal. The initial effort will consist of an evaluation and assessment of the compatibility, capability, and adequacy of deep and surface mines, oceans and other potential disposal sites for handling and disposal of untreated and/or chemically treated FGC wastes (sludges). The use of these wastes as soil amendments will also be assessed. Although environmental effects and operational safety will be the major initial consideration, the assessment will also include a study of the economics of the alternate disposal methods, as well as a study of applicable Federal and state regulations. Based on all of the initial efforts, recommendations and conceptual designs for the pilot demonstrations will be made.

The pilot demonstrations will be conducted at such a scale that design data for full-scale operations can be obtained. The mine alternative will probably consist of tests on small plots at an existing mine; the ocean alternative will consist of a tank which can simulate the ocean environment. The mine study will include monitoring for pollutants, characterizing pollutants, identifying limits of physical and chemical characteristics of wastes for disposal, and waste/mine interactions. The ocean study will include settling and dissolution characteristics and, in general, any parameters which would stress the ecosystem.

The initial assessment effort is nearing completion; a report on this effort is expected to be released by mid-1976. This assessment is based upon information, drawn from the published literature and from personal technical communications, on the chemical, physical, and mechanical (engineering) properties of both treated and untreated wastes. A key source of data has been the results of work conducted for EPA by Aerospace and the Corps of Engineers (WES). This data has been used to set a range of properties of wastes generated by lime, limestone and dual alkali scrubbing systems.

In the evaluation of FGC waste disposal in mines, an initial screening of the various types of mines in the U.S. was performed to group the mines into categories that would be amenable to a general assessment effort and

to identify the most promising candidates. The screening process resulted in the selection of six general categories of mines: active area strip coal mines; active underground coal mines; inactive or mined-out portions of active underground limestone mines; inactive lead-zinc mines; mined-out iron ore pits; and inactive or mined-out portions of salt mines. Characteristics of mines in each of these categories were reviewed to develop a set of typical environmental and operational conditions including hydrology, geology, climate, mine size and method of mining. As appropriate, these general categories have been further subdivided according to their general characteristics. Each group of mines was reviewed with regard to the alternatives for FGC waste placement, the physical properties of wastes that would be suitable, the capacity for FGC waste and the environmental/technical impacts of FGC waste disposal. Attention is also being given to the potential use of FCC waste (either treated or untreated) for subsidence control, as a tailings (soil) amendment and for neutralization or prevention of acid mine drainage.

The evaluation of the ocean disposal of FGC waste has focused on the Atlantic and Gulf Coast areas, since these regions are the most likely for FGC waste generation. The assessment includes both shallow (near shore) and deep ocean disposal with dispersed and/or bottom dumping of FGC waste. As in the evaluation of the impact of mine disposal, the ocean disposal assessment involves the determination of potential physical and chemical impacts. Special emphasis is being placed on the biological impact of ocean disposal, since the waste substrate and contaminants can be more readily available to marine organisms.

The EPA Project Officer for the project is the author of this paper. The ADL Project Director is Dr. Richard R. Lunt.

3.5 Utilization Technology Development

3.5.1 Lime/Limestone Scrubbing Waste Conversion Pilot Studies -

This project involves a cost-shared contract (currently being negotiated) with the M.W. Kellogg Company to conduct pilot studies of two key process steps in the "Kel-S" process for conversion of lime/limestone scrubbing waste

to elemental sulfur with recovery of the calcium in the waste as calcium carbonate. The effort includes (1) reduction of lime/limestone waste to calcium sulfide in a continuously rotating kiln, (2) dissolution of the kiln-produced calcium sulfide to calcium hydrosulfide using hydrogen sulfide from the calcium recovery unit, and (3) recovery (precipitation) of the calcium as calcium carbonate, using carbon dioxide-rich gas (available from the drying kiln), with simultaneous release of hydrogen sulfide, which can be converted to elemental sulfur (for disposal or sale) in a Claus plant. Separate pilot tests of the dissolution and recovery contactors will be made, followed by an integrated, continuous test using both contactors. Design data will be generated to allow scale-up to a large (prototype) test unit for a power plant. Assuming successful completion of the pilot testing and reasonable economics, this process would present a viable alternative to lime/limestone scrubbing waste disposal. The project, expected to get underway in the spring of 1976, will last approximately 11 months.

The EPA Project Officer for this project is the author of this paper. The Kellogg Project Director will be A. Glenn Sliger.

3.5.2 Fertilizer Production Using Lime/Limestone Scrubbing Wastes -

One of several tasks being conducted by TVA under an Interagency Agreement (EPA-IAG-D5-E-721), this project involves the use of lime/limestone scrubbing wastes as a filler material and a source of sulfur for fertilizer. This study is a continuation and expansion of previous bench-scale laboratory production tests and small field plot application tests with rye grass. Under the current effort, TVA will (1) conduct pilot plant tests of production of fertilizer using lime/limestone scrubbing wastes, (2) conduct tests of compatibility factors involved in storage and mixing of this fertilizer material with conventional fertilizer, (3) conduct field plot tests using fertilizer from the pilot plant, (4) conduct economic/marketing studies, and (5) determine the amounts of trace and/or toxic elements in this fertilizer and compare them with those in conventional fertilizer. Initial pilot plant production and storage/compatibility tests are expected to be completed by mid-1976. The project is expected to be completed by mid-1979.

In the initial pilot production tests, severe chemical difficulties were encountered when scrubbing waste was introduced into the preneutralizer portion of the fertilizer granulation unit. (The preneutralizer is the equipment into which ammonia and phosphoric acid are introduced.) When the waste was fed to the drum granulator (the preneutralizer outlet stream, or ammonium phosphate melt, was fed to the granulator via a separate system), the pilot plant still did not operate satisfactorily because of the excess moisture in the waste. It is felt that development and testing of a new preneutralizer design will be necessary to alleviate the problems encountered so far; these efforts are currently underway.

The EPA Project Officer for this project is the author of this paper. The TVA Project Director is James L. Crowe.

3.5.3 Use of FGD Gypsum in Portland Cement Manufacture -

This project will consist of the following efforts: (1) laboratory tests at a portland cement manufacturing plant to determine the possible range of variability in the chemical quality and physical characteristics of FGD gypsum which can be used, so that recommendations can be made for operational changes either in the FGD system or the cement plant; (2) pilot testing of FGD gypsum physical and/or chemical conditioning and portland cement manufacture using the gypsum product; and (3) a test program involving full-scale FGD equipment (possibly including FGD waste oxidation equipment) at a coal-fired utility power plant and a full-scale portland cement manufacturing facility. Reports will be issued after completion of each of the efforts described. The project is expected to get underway by mid-1976, and is expected to be completed by mid-1979.

The EPA Project Officer for this project is the author of this paper. The contractor for this effort will be announced in the near future.

3.5.4 FGD Waste/Fly Ash Beneficiation Studies -

This project will consist of the following efforts: (1) a conceptual design/cost study of a TRW-conceived, proprietary process (for which two related patents have been issued) for producing sulfur, alumina, and dicalcium

silicate for FGD waste and fly ash (and/or clay), including the development of a preliminary process design (including material and energy balances) and an estimate of capital and operating costs to determine the economic viability of the process; (2) if the economics of the process appear favorable, a bench-scale laboratory investigation to determine probable ranges of operating conditions for each of the major processing steps (reduction, calcination, leaching, separation) and to determine (with actual FGD waste) probable yields and purity of products; (3) assuming the process still appears viable, possible pilot scale testing of the process steps to obtain design data for large-scale equipment. Reports will be issued after each of the efforts described above.

The conceptual design/cost study is expected to be underway in the very near future; this effort will take approximately 4-6 months to complete. The bench scale tests should be initiated in early 1977.

The EPA Project Officer for this project is the author of this paper; the TRW Project Director will be Dr. Jack Blumenthal.

3.6 Power Plant Water Use

This effort consists of a contract (68-03-2339) with Radian Corporation, who will conduct a study on minimizing water use and waste water discharges from coal-fired steam-electric power plants. The study will consist of six tasks: (1) Plant selection and characterization--selection of three or more specific plants for detailed analysis; collection of detailed data on make-up, process, and effluent waters, plant design, operation modes, coal composition and climate for each plant. (2) Process model preparation--preparation of computer models to simulate make-up, process, and effluent water streams, and chemical equilibria of the processes for each of the specific plants selected for detailed study. (3) Simulation of existing plant operations--verification of process computer models by comparing existing plant chemical and operating data with data predicted by the models. (4) Technical assessment of recycle/reuse options--formulation of a number of water recycle/reuse options to minimize plant water requirements and discharges for the specific plants selected for study; evaluation of at least one option (via

process simulation) for each plant. (5) Cost estimates--preparation of capital and operating cost estimates for each viable water recycle/reuse option. (6) Recycle/reuse assessment report--detailed presentation of program results, including recommendations of the recycle/reuse options to be used at each of the plants studied. Current plans call for completion of this effort in late 1976, followed by pilot plant testing of one or more of the recycle/reuse options at a coal-fired power plant.

Currently, three plants are being studied under the project--Four Corners (Arizona Public Service), Comanche (Colorado Public Service) and Bowen (Georgia Power). Water samples from selected streams have been taken at each of the plants; chemical analysis of these samples has recently been completed. Simulation of existing plant operations will be made in the near future, after computer program modifications have made to simulate the equipment arrangements at specific plants.

The EPA Project Officer for this project is Fred A. Roberts of the Industrial Environmental Research Laboratory, Research Triangle Park, N.C. Mr. Roberts is currently located in Corvallis, Oregon. The Radian Project Director is Dr. Delbert M. Ottmers.

4.0 CONCLUSIONS AND FUTURE PLANS

The main thrust of future activities under the FGC Waste and Water Program is continuation of the efforts described above. In summary, this means that the environmental/technological assessment and economic efforts will be pursued to logical conclusions, and that development of promising FGC waste disposal/utilization alternatives and power plant water use technologies will also be pursued. However, because some of the technology in the area of FGC waste disposal/utilization is only in the developmental stage, emphasis is expected to shift to those projects with the greatest promise of success. This shift in emphasis may create new projects in areas which are not not being intensively studied; e.g., modifications within the FGD process to change the physical/chemical characteristics of the waste solids.

The current FGC Waste and Water Program is a comprehensive program designed to reduce the environmental and economic impact of power plant waste

and water pollution controls. Results from efforts under this program will provide alternative strategies which can be applied to a fairly broad range of power plant situations. However, application of the results could be strengthened and broadened if additional funding were applied to the pilot/demonstration phases of several projects. Sources of these funds could include private industry, the Electric Power Research Institute (EPRI), and other government agencies. In this regard, discussions are now being held with EPRI to determine those areas where joint financial support of projects would be most fruitful. Although specific projects have not yet been identified, the FGC waste utilization area is a likely candidate.

A main part of the significance of this program, in the author's opinion, is that it sponsors research and development for which there is, at least initially, little or no financial incentive to private industry. More importantly, results from this program can accelerate the increasing use of domestic coal supplies in fossil fuel-fired power plants; this is an important part of the nation's energy objectives.

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FLUE GAS CLEANING WASTE DISPOSAL
EPA SHAWNEE FIELD EVALUATION

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ABSTRACT

This paper summarizes the first year's results (1974-1975) of the EPA's on-going Flue Gas Cleaning (FGC) Waste Disposal Field Evaluation Project at the TVA Shawnee Steam Plant in Paducah, Kentucky. In this project, five different disposal ponds containing lime or limestone flue gas scrubbing waste from two 10-MW (equivalent) prototype scrubber systems (i.e., a Chemico venturi/spray tower and a UOP Turbulent Contact Absorber) are being evaluated. Two of these ponds contain untreated wastes, and each of the other three contains waste treated by one of three different commercial chemical fixation processors: Chemfix, Dravo, and IU Conversion Systems. This paper discusses initial results of analyses of leachate, supernate, and ground waters from all ponds, and physical properties of fixed waste cores taken from the disposal site. Based on data obtained from these evaluations and from correlations of these data with long-term laboratory analyses at Aerospace, projections are made that show orders-of-magnitude reductions of leachate total dissolved solids as a result of reducing the solubility and permeability of the FGC wastes and of minimizing the recharge of water to the disposal site. Additionally, total fixation-disposal cost studies were made, resulting in estimates of \$7.30 to \$11.40 per ton of waste (on a dry basis).

FLUE GAS CLEANING WASTE DISPOSAL - EPA SHAWNEE FIELD EVALUATION

1.0 INTRODUCTION

The Environmental Protection Agency (EPA) has initiated a power plant site field evaluation of the disposal of untreated and treated flue gas cleaning (FGC) wastes for the purpose of verifying the effects of several disposal techniques and scrubbing operations, soil interactions, and field operation procedures on the environmental acceptability of the disposal site. The program began in September 1974 and is scheduled to continue to mid-1977. The principal objectives of this program are as follows: (1) evaluate current disposal techniques under representative field operating conditions; (2) evaluate the environmental acceptability of current disposal technology through periodic sampling, analysis, and assessment of water, soil, and waste cores; and (3) develop engineering cost estimates for alternative disposal methods on an operational basis.

The Tennessee Valley Authority (TVA) Shawnee Power Station at Paducah, Kentucky, was chosen as the site for the evaluation. Two different scrubber systems (i.e., a UOP Turbulent Contact Absorber and a Chemico venturi followed by a spray tower, using limestone and lime, respectively, as the SO₂ absorbent) upstream of fly ash collection are being operated at this station as an EPA/TVA test facility. Each scrubber system is capable of independently treating up to 10 MW (equivalent) of flue gas from one boiler (approximately 30,000 ft³/min at 300°F). Wastes from these scrubbers are being used in the disposal evaluation and are undergoing analysis in several laboratories under EPA sponsorship.¹⁻⁵ Related laboratory analyses are being conducted under EPA contract by Mahloch et al.⁶

The disposal evaluation site consists of five disposal ponds, each occupying approximately 0.1 acre near the Shawnee plant and approximately one mile south of the Ohio River (see Figure 1). All are six feet deep and have been filled with FGC wastes to a depth of approximately three feet. Two of the ponds contain untreated wastes; each of the remaining ponds contains wastes chemically treated by one of the three commercial contractors. The surfaces of the three treated ponds are sloped to create a wet section consisting of a combination of liquor and rainwater, and a potential dry section (depending on weather conditions) for the observation of physical conditions of dry material. Within each pond is a four-inch-diameter plastic pipe leachate well that collects water samples at the waste-soil interface. A ground water well is located on a berm of each pond, between the sludge and the river, and a ground water well is located approximately 100 feet south of each pond (away from the river) to provide monitoring of background water quality. The disposal sites are being monitored periodically for leachate, supernate, and ground water quality; soil chemistry changes; and treated waste chemical and physical qualities.

It should be noted that each of the three treated ponds was conditioned and filled by the respective contractors in response to program requirements so that various operational conditions and the effects of weather could be evaluated. These operations, therefore, do not represent identical disposal conditions or necessarily the operational methods that would be employed by any of the contractors. For example, different input materials were supplied to the contractors; the ponds are not provided with drainage so that the effects



Figure 1. Overview of disposal site

of trapped water can be observed; one treated material (Chemfix) was fractured and contoured by a back hoe; one (Dravo) represents curing and disposal underwater where high strength is not necessarily required; and one (IUCS) was not compacted by placement vehicles that would be used in a full-scale operation. Therefore, comparisons between processes are neither attempted nor implied in these evaluations. The principal environmental factors being observed are the quality of seepage water, and the strength and permeabilities of the fixed materials. Correlations are being made between laboratory-prepared samples and those created under field operating conditions. Additionally, results obtained are being used to form a basic understanding of the major characteristics of field operations, estimate total costs, define procedures for planning additional evaluation at this site, and assist in the development of other EPA-sponsored field evaluations.

This program is managed by the EPA Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. The Aerospace Corporation provides program coordination, program plans, selected analyses, analytical results, costing estimates, and reporting. TVA provides for all construction, filling of untreated ponds, supplying wastes to fixation processors at the site, maintenance, sampling and analyses, sample distribution, climatological and hydraulic data collection, and photographic documentation. The waste fixation processors are Chemfix, Inc., Pittsburgh, Pennsylvania; Dravo Corporation, Pittsburgh, Pennsylvania; and IU Conversion Systems, Inc. (IUCS), Philadelphia, Pennsylvania. The Bechtel

Corporation (the scrubber facility test director) provides the technical interface relating the scrubber test facility to the disposal evaluation.

A detailed description of this program, and results of the first year's work are given elsewhere.⁴ Highlights of these results are presented herein.

2.0 POND FILLING AND FIXATION

The five disposal ponds were filled between 7 October 1974 and 23 April 1975; the characteristics of the fill material are as shown in Table 1.

Table 1. CHARACTERISTICS OF POND FILL MATERIALS

Pond	Scrubber Type	Waste Absorbent/Source	Solids Content (Untreated), wt%	Treatment Contractor
A	Venturi/Spray Tower	Lime/Filter Cake	46	Untreated
B	Turbulent Contact Absorber	Limestone/Clarifier	38	Dravo
C	Venturi/Spray Tower	Lime/Centrifuge Cake	55	IUCS
D	Turbulent Contact Absorber	Limestone/Clarifier Underflow	38	Untreated
E	Turbulent Contact Absorber	Limestone/Clarifier Underflow	38	Chemfix

The operation associated with the filling of each pond is described in the following sections.

2.1 UNTREATED PONDS (A and D)

2.1.1 Pond A. Pond A was filled between 24 September and 8 October 1974 with untreated waste from the venturi/spray tower scrubber in which lime was used as the absorbent. The waste had been dewatered by filtering and had a solids content of 46 wt% when it was placed in the pond. Ash constituted approximately 43 wt% of the solids. A rotary drum mixing truck was used to haul the waste to the pond in order to maintain a homogenous mix during loading and transportation. Dispersal of the waste in the pond was achieved by dumping the waste at various locations in the pond from which it was allowed to settle and seek its natural level. The condition of the waste in Pond A one month after filling is shown in Figure 2. Rainwater accumulated on the pond over the next few weeks, as shown in Figure 3.



Figure 2. Pond A one month after filling



Figure 3. Pond A two months after filling

2.1.2 Pond D. Pond D was filled twice, i.e., from 11 to 20 October 1974 and from 13 January to 5 February 1975. The material used in the first filling was subsequently transferred to Pond E; during the transfer the material was chemically treated by Chemfix. The waste used for both fillings was clarifier underflow from the Turbulent Contact Absorber, with limestone as the absorbent and a solids content of 38 wt%. Likewise, on both occasions, ash represented approximately 38 wt% of the solids. For both fillings, a rotary drum mixing truck was used to transport the waste to the pond, and dispersal was as described for Pond A. The condition of Pond D two months after the second filling is shown in Figure 4.



Figure 4. Pond D two months after second filling

2.2 TREATED PONDS (B, C, and E)

The materials used in the evaluation of chemical fixation represented various disposal operating conditions. Pond B was filled using clarifier underflow chemically treated by Dravo and placed in the pond under conditions approximating disposal behind a dam. Pond C was filled using waste that had been dewatered by centrifuging, fixed by IUCS, and stored in the pond under conditions representing a landfill. Pond E was filled with clarifier underflow chemically treated by Chemfix and placed in the pond under conditions representing a landfill. Liquor on the surface and rainwater were allowed to remain in these ponds to represent a low spot in a landfill from which water does not readily drain. The operations associated with the filling of each of these three ponds were as follows.

2.2.1 Pond B (Dravo). Pond B was filled from 7 to 15 April 1975. The effluent delivered to Dravo was limestone clarifier underflow from the Turbulent Contact Absorber. The waste was 38 wt% solids, and the solids contained 40 wt% ash. Dravo received the effluent from the clarifier, used a rotary drum mix truck for transportation, and added the Dravo proprietary additive (Calcilox®) to each truck load from 55-gal drums through the use of a fork lift. The amount of Calcilox® added represented approximately 11 wt% of the dry solids being treated. The waste settled to approximately 45 wt% solids and stabilized at a rate controlled by the Calcilox® content.

Because of the small scale and temporary nature of the project, the treated waste was dumped directly into Pond B and allowed to settle and cure under the supernate and subsequent rainwater. Under normal field conditions, the supernate would be returned to the scrubber loop. Views of Pond B six days and two months after filling are shown in Figures 5 and 6, respectively. Solids can be seen in the foreground in Figure 5.

The purpose of this process is to treat wastes of various solids content. It produces a material that resembles cemented soil in consistency for use as a material for landfill, either by mechanical compaction or by stabilization behind a dam. (Dravo recommends Ref. 7 for further information on their process.) Pond B simulates the latter condition, except, as noted, there is no recirculation of the supernate in the Shawnee evaluation. In this evaluation, Calcilox® was prepackaged for 10 to 11 percent additive based on an expected waste solids content of 35 wt% and diluted further by pump seal water. Based on the experience gained at Shawnee and their laboratory data, Dravo recommend a 7.5 wt% (dry basis) additive for a full-scale operation using Shawnee-type waste, with an assumed average of 38 wt% solids.

2.2.2 Pond C (IUCS). Pond C was filled from 31 March to 23 April 1975. The waste delivered to IUCS was from the venturi/spray tower scrubber (using lime as the absorbent) and was clarifier underflow dewatered by a centrifuge. The average solids content was 55 wt%, and the ash comprised 45 wt% of the solids. The centrifuged waste was conveyed to an IUCS-operated rotary drum mixer truck and transported to the pond site where additive was mixed with the waste prior to discharge into the pond.

The IUCS process produces a material identified as Poz-O-Tec®, which has applications as landfill, as well as variations of this material for other structural applications.⁸⁻¹¹ In the Shawnee field evaluation, IUCS used a lime additive premixed with fly ash. (The quantity of lime is dependent on the moisture content of the waste and the reactivity of the fly ash already contained in the FGC waste.) The waste solids content ranged from 47.5 to 59 wt%, and the average quantity of lime additive was approximately 4.8 wt% of the dry solids being treated plus approximately an equal amount of fly ash. Delivery of the treated waste to the disposal site by truck is generally the transportation mode recommended by IUCS for a full-scale disposal operation under conditions similar to those of the Shawnee evaluation.

A significant benefit claimed for this method of fixation is low permeability (as well as reduced solubility). In this evaluation, the waste was dispersed by manual raking; some degree of compaction was achieved by this process. Dispersal and compacting methods appropriate to handling large quantities would be required in a full-scale operation. Figures 7 and 8 show Pond C three days and three months after filling, respectively.



Figure 5. Pond B six days after filling

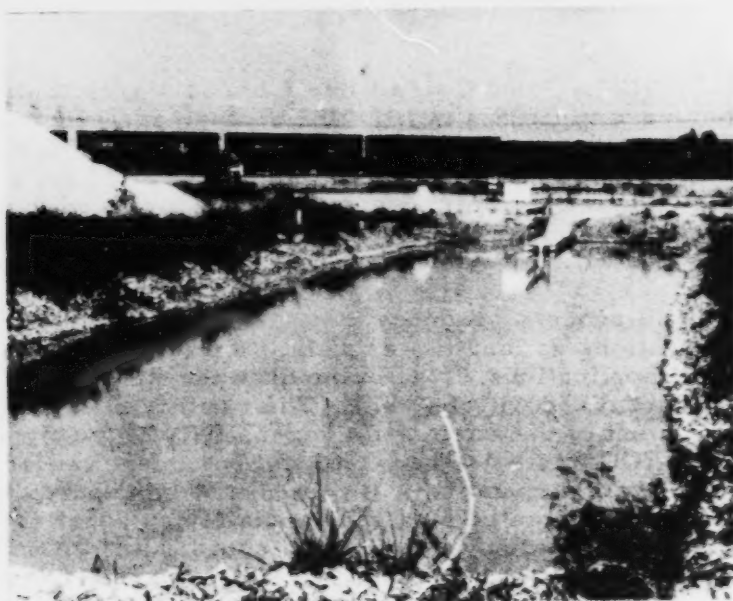


Figure 6. Pond B three months after filling



Figure 7. Pond C three days after filling

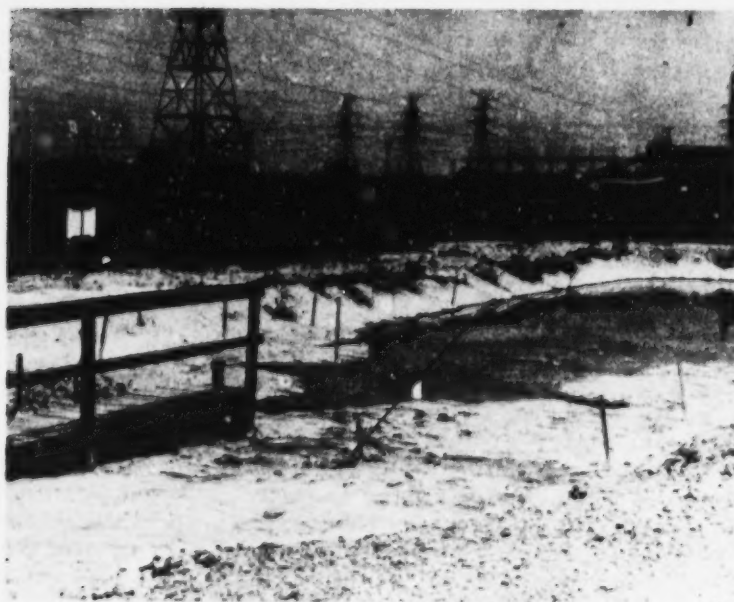


Figure 8. Pond C three months after filling

IUCS has reported that the addition of dry fly ash is not mandatory, nor is it planned for full-scale operations when fly ash is present in the wastes as is the case at Shawnee. It was also reported by IUCS that, when their process is used to treat an FGC waste such as that used at Shawnee and when the treated waste is disposed of in a managed landfill, the lime additive will be in the range of 1 to 4 wt% (dry basis).

2.2.3 Pond E (Chemfix). Pond E was filled between 3 and 7 December 1974 using the waste stored in Pond D as input material. This waste was clarifier underflow from the Turbulent Contact Absorber in which limestone was used as the absorbent. The solids content was 38 wt%, and ash constituted 38 wt% of the solids. The waste stored in Pond D was thoroughly mixed before it was pumped from the pond into a Chemfix processing trailer and then pumped into Pond E (see Figure 9). The Chemfix process used the reaction of sodium silicate and portland cement with the waste to stabilize it. Approximately one month after filling, the material was contoured with a back hoe by TVA field personnel so that it would more evenly cover the pond surface and so that an evaluation could be made of a fixed material that had been fractured and moved by heavy equipment (see Figure 10).

The Chemfix process is designed to handle waste fixation over a broad range of percent solids and produces a material having a soil-like appearance. Furthermore, it is not designed to prevent the percolation of water but rather to bind the constituents chemically to accomplish pollution control while also providing structurally stable properties.¹²⁻¹⁶

In accordance with the specification provided Chemfix for the Shawnee evaluation, they treated clarifier underflow. In their process, the amount of additives is significantly affected by the moisture content of the wastes and the degree of drainage of the landfill. For the Shawnee evaluation, with 38 to 40 wt% solids and the treated waste in an undrained landfill, Chemfix reported that the additives required were 46 wt% of the dry solids content. Chemfix also reported the following: (1) If the water in the pond above the treated material were removed, the additive required to achieve an equivalent condition would be reduced to 39 wt%; (2) Dewatering of the waste to 50 wt% solids would reduce additive requirements to approximately 15 wt% of the dry solids content; and (3) Dewatering to 55 wt% solids would further reduce the additive requirements to about 9 wt% of the dry solids content.

3.0 ANALYTICAL RESULTS

Considerable data have been determined from analyses of input FGC wastes, supernate, leachate, ground water, and soil and fixed material cores. The most significant of these data as regards environmental impact are the quality of leachate and ground water, and the strength and permeability of the fixed wastes; therefore, these analyses are emphasized in the following sections. Data available are discussed, and as the project progresses, these data will be expanded and correlated with other available laboratory and field evaluation data.

3.1 UNTREATED WASTES

For Pond A, which contains untreated waste, the data obtained from leachate samples to date show that the concentrations of the dissolved solids,

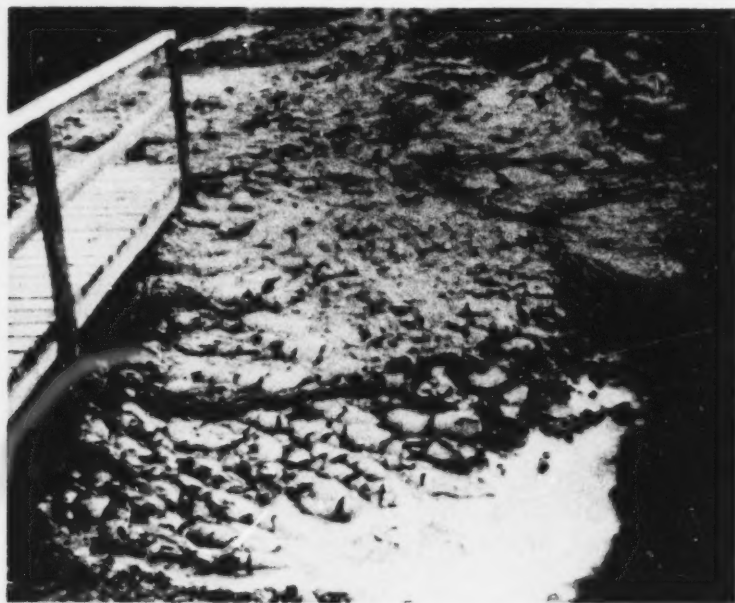


Figure 9. Pond E during filling, before contouring

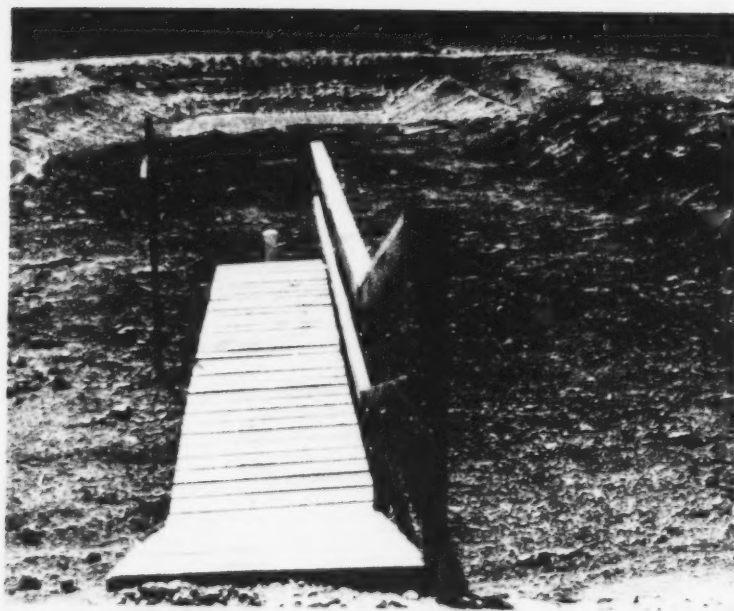


Figure 10. Pond E five months after contouring

i.e., Cl , SO_4 , and total dissolved solids (TDS), progressively increase with time (see Figure 11). The data also indicate that the concentrations may level off at approximately those measured in the input liquor. Simultaneously, the concentrations of these same constituents in the pond supernate vary with time. Neither the scrubber system waste solids nor liquors are replenished, therefore, the supernate should become increasingly diluted with rainwater as the program progresses. Some fluctuation in this trend can be expected as a result of evaporation during dry periods. The detection of heavy metals in the leachate and supernate of this pond shows trends similar to the major species, however, concentration projections are not as easily made because of the relatively small magnitude of the values (see Figure 12). Continued field monitoring is expected to produce data that will define concentrations and mass released to the soil with respect to time. As regards pH of the leachate, the first year's monitoring of both untreated ponds has shown a decrease to 7 from the initial range of 8 to 9.

Pond D, the other untreated pond, was filled in October 1974 and was used as the input source of material for the Chemfix operations at Pond E in December 1974. At that time, approximately 75 percent of the waste from Pond D was removed. The pond was refilled with a similar waste in February 1975. The removal and refilling of this pond have produced some discontinuities in the initial data such that projections are not as easily made as for Pond A. Leachate dissolved solids concentrations are shown in Figure 13 for this pond starting with the second filling. The accumulation of additional data will continue throughout the program to produce more accurate trends.

Analyses of samples of ground water (approximately 12 feet below Pond A and 40 feet below Pond D) have not shown any effect of seepage from these ponds.

3.2 TREATED WASTES

The data from the ponds containing treated wastes, although sampled over a shorter period of time, show trends similar to those of the untreated waste, except the reductions of concentrations due to chemical fixation are evident in the leachate analyses. Indications are that these concentrations either start at or quickly build up to (depending on the amount of rainwater present in the well initially) approximately 50 percent of the respective concentrations in the liquor of the untreated input waste (see Figures 14, 15, and 16). The long-term results of these field evaluations will be studied and reported throughout this project.

A sample laboratory leachate analysis for long-term TDS concentrations of an untreated Shawnee limestone scrubbing waste and of a core taken from a treated pond at the Shawnee disposal site is shown in Figure 17. This treated pond contains limestone scrubber waste and has been in operation for the longest time period of the three treated ponds, approximately one year. In these analyses, distilled water was allowed to seep through the pores of the samples, and chemical analyses of the collected leachate were made periodically. Figure 17 shows the variation of TDS concentration as a function of pore volume displacement of leachate water (pore volume in this case is the nonsolid volumetric portion of a given mass). These trends are generally typical for the various constituents of the materials, including trace elements.^{4,5} Measurement of the pH of leachate from the treated ponds has exhibited a

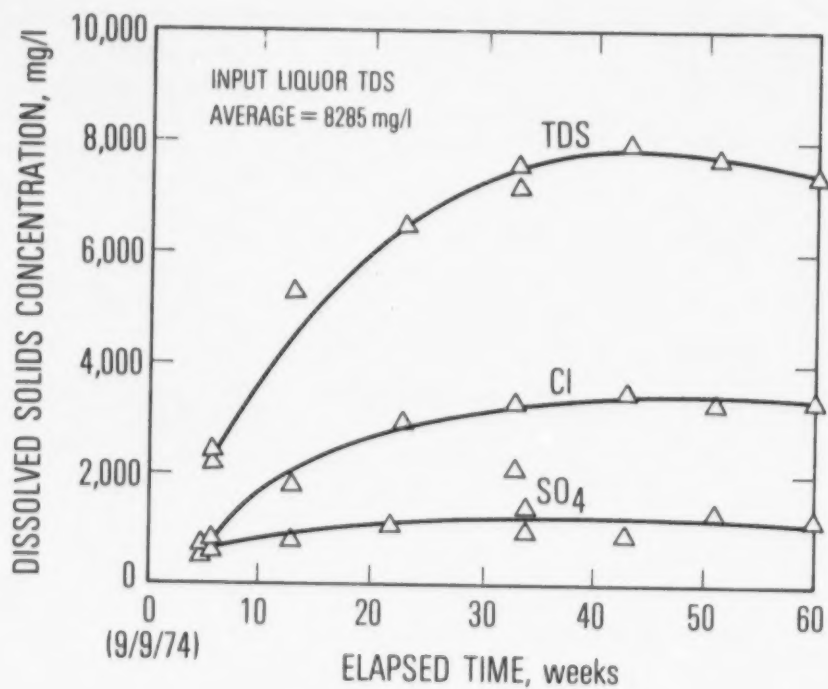


Figure 11. Pond A leachate dissolved solids

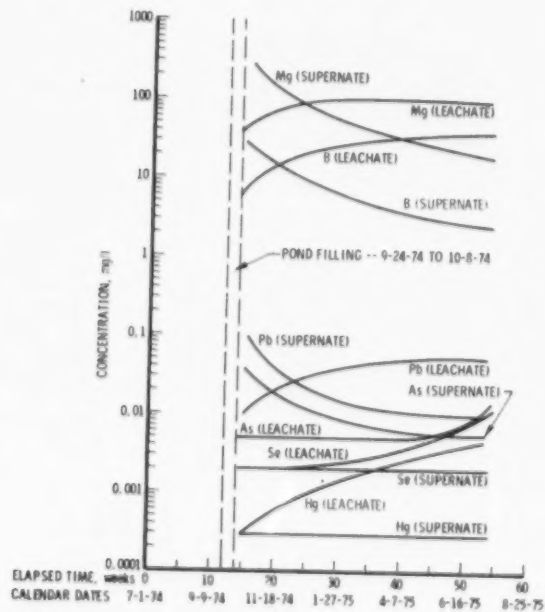


Figure 12. Minor constituents of Pond A supernate and leachate

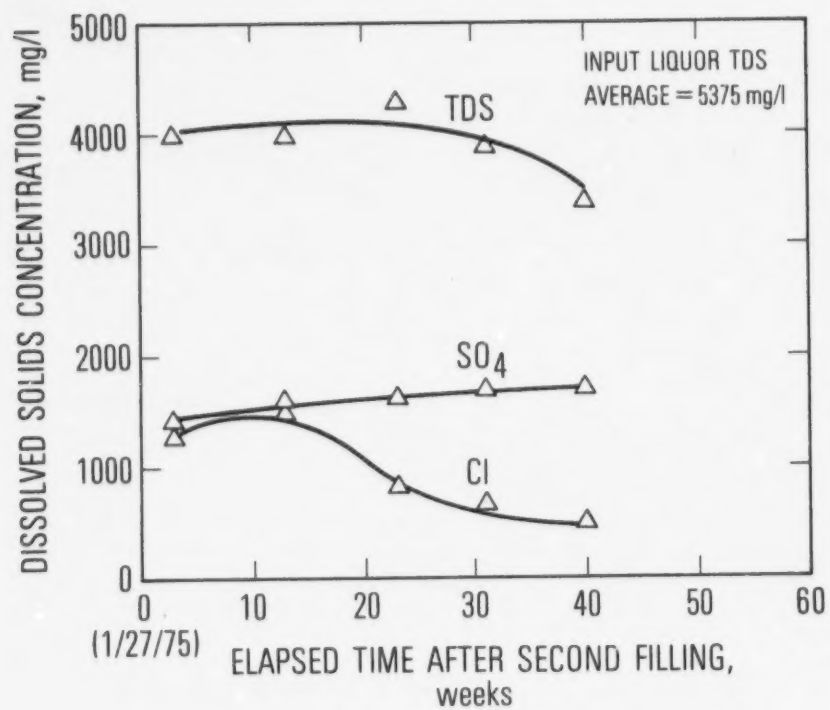


Figure 13. Pond D leachate dissolved solids

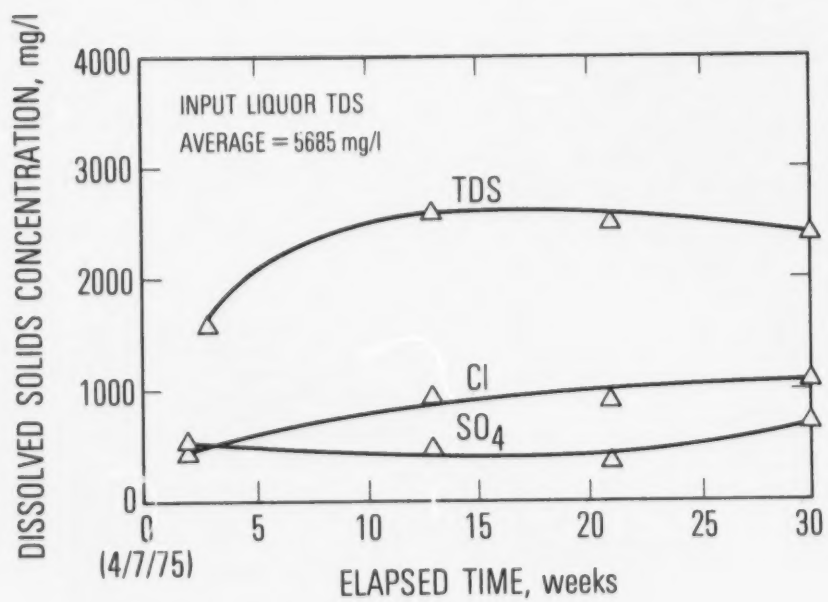


Figure 14. Pond B leachate dissolved solids

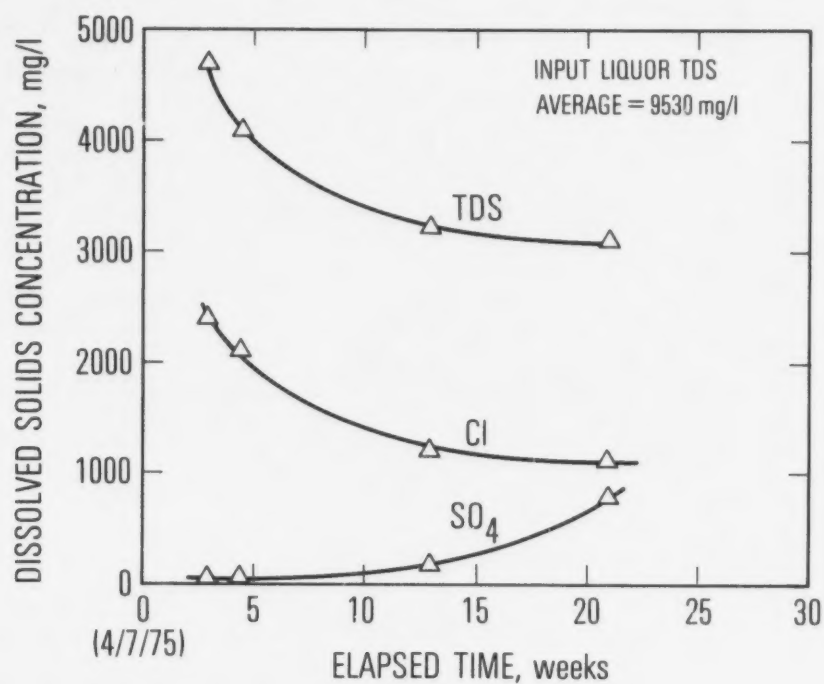


Figure 15. Pond C leachate dissolved solids

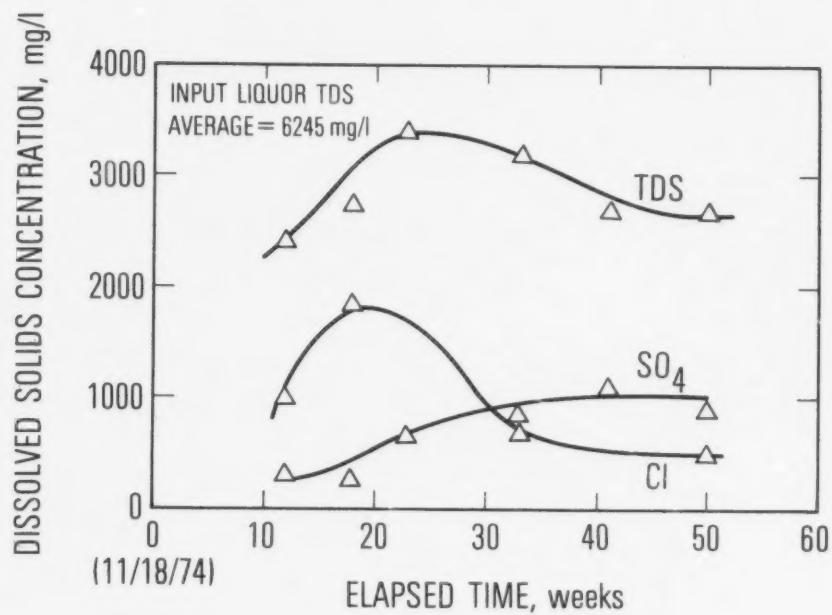


Figure 16. Pond E leachate dissolved solids

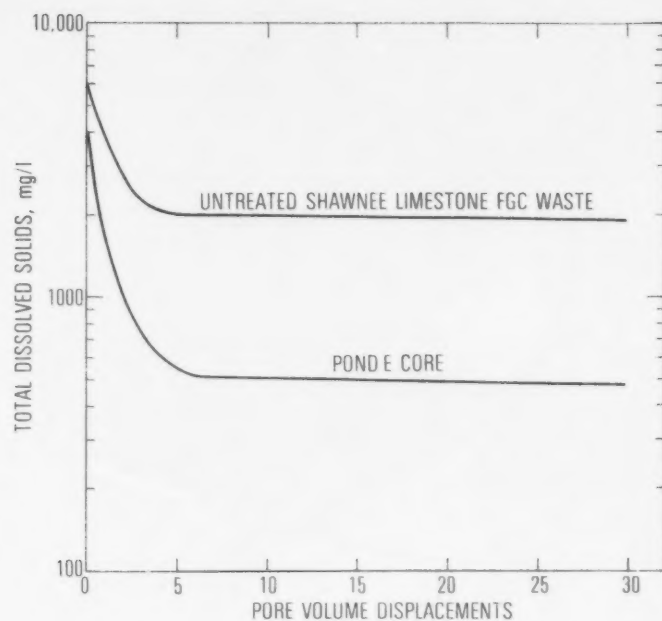


Figure 17. Laboratory leachate analyses of treated and untreated FGC wastes showing the effect of leachate pore volume displacement on TDS concentrations

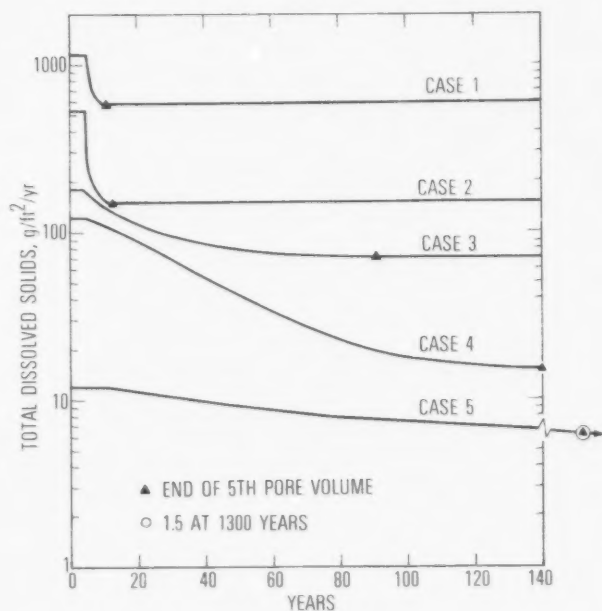


Figure 18. Mass loading of TDS to subsoil for various disposal modes of treated and untreated FGC wastes

decrease to values of 9 to 10 from a range of 11 to 12 during the first six-month period. Based on laboratory column data, pH is expected to stabilize at approximately 8, where it is believed to reflect the buffering action of the carbonate ion.

Several significant characteristics are shown in the data presented in Figure 17. First, both materials, treated and untreated, display a steep drop in leachate TDS concentration during the first five pore volume displacements. During this period, salts from the waste liquor trapped within the pores are flushed out. Thereafter, solubility of the sulfite, sulfate, and chloride within the solid mass becomes one of the controlling parameters. Another point of interest is that the time to achieve five pore volume displacements is not the same for the two materials. Because the permeability rate of the treated material is at least one order of magnitude lower than that of the untreated material, the time scale for that event is significantly retarded. The effect of time is shown in Figure 18. A third significant point is that, after the initial flushing period, the leachate and the TDS concentrations have stabilized to about 1900 ppm for the untreated and 500 ppm for the treated; this represents a reduction of concentration of the leachate from treated material to about 25 percent of the untreated.

The combined effects of all these factors are shown in Figure 18. It represents some initial results from an analysis being conducted to project data such as that shown in Figure 17 to operational conditions and to time periods well beyond the end of this project. Because a treated disposal site releases leachate to the subsoil over a longer time period and at smaller concentrations than an untreated disposal site, the purpose of this analysis is to make comparisons between treated and untreated materials in terms of the mass per unit area of dissolved solids released to the subsoil as a function of time. In Figure 18, five sample cases shown in Table 2 are plotted based on

Table 2. INPUT DATA FOR STUDY CASES

Case	Disposal Mode	Surface Water	FGC Waste, 5-Year Fill			
			Waste Condition	Depth, ft	Permeability (C_p), ^b cm/sec	Fractional Pore Volume
1	Lake ^a	Constant Supernate	Untreated	30	10^{-4}	0.67
2	Lake ^a	Constant Supernate	Treated	30	10^{-5}	0.67
3	Pond	10 in./yr Recharge	Untreated	30	10^{-4}	0.67
4	Pond	10 in./yr Recharge	Treated	30	10^{-5}	0.67
5	Landfill	1 in./yr Recharge	Treated	30	10^{-5}	0.67

^a Assumed maximum hydraulic head of six feet during filling, including depth of wastes. One foot constant water cover thereafter.

^b For all cases, subsoil $C_p = 10^{-5}$

the data in Figure 17. The advantages of reducing the permeability and the solubility of the wastes, and of preventing water from accumulating on the surface, are highlighted in this figure. For example, for the first 100 years, a treated material in a landfill with controlled runoff (Case 5) releases approximately one-hundredth the mass of dissolved solids at a given rate to the subsoil as an untreated material in a lake (Case 1), and approximately one-tenth as much as an untreated material in a pond (Case 3). Years to reach five pore volume displacements (initial drainage period) are also shown.

Leachate analyses such as those discussed above are being continued; more specific operational parameters will be applied, and the results related to disposal criteria that may evolve during this project. Although some methods of disposal produce much less release of mass to the subsoil than others, this is not to indicate that the methods with the lower release rates are the only acceptable approaches. Criteria for judging disposal methods are being determined by the EPA and will be applied when they are available.

Some preliminary physical properties of the fixed wastes are given in Table 3. Of particular interest are the permeabilities (6.9×10^{-5} to 5.5×10^{-7} cm/sec) and unconfined compressive strengths (3 to 39 ton/ft²). Analyses for these properties will be made on cores taken from the treated ponds periodically throughout this project. FGC wastes that have not been treated or conditioned have a permeability coefficient of approximately 10^{-4} cm/sec and no practical structural strength. The effects of conditioning untreated wastes, e.g., dewatering and compaction, are being studied.

4.0 SOIL

As noted earlier, the ground waters show no evidence of altered quality resulting from the filling of any of the five ponds. This result is in agreement with expectations based upon the very low permeabilities measured on clay soil samples from the floor of the ponds. Analyses conducted by TVA show a typical permeability in the range of 10^{-8} cm/sec for these soils. Thus far, the waste leachate constituents would be expected to permeate to a depth of less than 0.5 inches. Laboratory analyses using an ion microprobe mass analyzer are underway to detect the progress of the constituents in successive soil cores in order to verify long-range analytical predictions over a relatively short time period, i.e., within the time span of the evaluation program. At this point, the initial calibration runs have been completed on pond floor core samples to provide background data for soils analyses.

5.0 TOTAL DISPOSAL COST ESTIMATES

In order to assess the economics of the cross section of chemical treatment and disposal modes and variations in effluent conditions such as ash and solids content, engineering estimates were requested from Chemfix, Dravo, and IUCS for the estimated cost of full-scale operations. The Shawnee field evaluation experience provided a basis to relate processing variables to the costs of an operation treating and disposing of 125 ton/hr (dry basis) of waste, including fly ash, from a 1000-MW power plant. Typically, the solids in the wastes supplied to the processors consisted of approximately 45 wt% fly ash, and 45 to 50 wt% sulfite and sulfate (in a 3 to 1 ratio), with the remainder being unreacted limestone or precipitated calcium carbonate.

Table 3. CHARACTERISTICS OF CORES FROM CHEMICALLY FIXED FGC WASTES

Source	Unconfined Compressive Strength, psi		Density, g/cm ³		Water Content, wt%	Estimated Fractional Pore Volume	Water Permeability, cm/sec
	Wet ^a	Dry ^b	Wet ^a	Dry ^b			
Pond E ^c (2/27/75)	103-133	95-165	1.40-1.46	0.69-0.73	51.0-51.5	0.71-0.73	1.5-2.7 × 10 ⁻⁵
Pond B ^d (6/12/75)	27-33	40-46	1.36-1.44	0.59-0.62	56.9-57.8	0.75-0.76	6.9 × 10 ⁻⁵
Pond C ^c (5/29/75) (6/12/75)	410-510	470-540	1.67-1.70	1.05-1.08	36.5-37.0	0.57-0.58	5.5 × 10 ⁻⁵ 5.5 × 10 ⁻⁷

^aWet: as received.

^bDry: after oven drying.

^cSamples from Ponds E and C were taken from locations free of surface water.

^dPond B material is kept underwater continuously as in the case of disposal upstream of a dam.

Capital and operating costs for the full-scale projections were presented by the fixation contractors, including items such as capital investment, additives, labor, processing, and transportation, with disposal of the fixed material at sites both 0.5 and 5.0 miles from the power plant. Costs in terms of dollars per ton of dry waste disposed were provided. Those costs were evaluated and adjusted by Aerospace to produce estimates of total disposal costs on a common basis as much as possible. Major steps taken were as follows: (1) annualized 30-year average capital charges of 18 percent were used in all cases, (2) land at \$1000/acre and dewatering costs were added as appropriate, (3) transportation and site preparation costs were adjusted as appropriate, and (4) all costs were adjusted for 30-year average annual load factors of 50 and 65 percent.

Considering all three processes, the Aerospace-adjusted total cost for fixation and disposal of the FGC wastes (using a 50 percent load factor and a 5-mile disposal site) is in the range of \$7.30 to \$11.40/ton of waste (dry) in 1975 dollars. If it is assumed that coal is burned at a rate of 0.88 lb/kW-hr, the total disposal costs for this Shawnee-type waste are \$2.07 to \$3.24/ton of coal. This cost equates to 0.9 to 1.4 mil/kW-hr. An average cost reduction of approximately 7 percent can be attained in this analysis by increasing the average load factor from 50 to 65 percent, and approximately 9 percent by using a disposal site 0.5 miles from the plant instead of 5 miles. Detailed background data related to these results are given elsewhere.⁴

Because these cost data are based on types of plants and operations that are not universally applicable, no attempt was made to rank the disposal costs for the three processes being evaluated. As a result of this evaluation, however, these data provide a range within which the total cost of FGC waste fixation and disposal may be expected.

5.1 OTHER COST CONSIDERATIONS

The engineering estimates provided are considered to be representative of the cost of disposal by fixation. Some factors that could affect disposal costs somewhat but are highly site-dependent were omitted. These include access roads and rights-of-way whose costs may be offset by the residual value of the land. Also, credit for the cost of fly ash disposal was not applied in this study. Consideration will be given to that factor in follow-on assessments of the cost impact of FGC waste disposal over current waste disposal costs. Another approach that may have merit in reducing disposal costs is the removal of fly ash prior to scrubbing and, in some cases, reintroducing it after the scrubber waste is mechanically dewatered. An appreciable increase in the percent solids would result, thereby reducing the following: (1) fixation additive requirements, (2) the total mass of material to be treated and handled, and (3) the acre-feet of disposal site required. Cost trade-off studies to evaluate these effects will be made as this project progresses.

6.0 PLANS

Plans are being implemented to make two modifications to the Shawnee Scrubber Program to (1) include an oxidation unit that can be used to convert sulfite wastes to gypsum, and (2) incorporate a flue gas by-pass so that fly ash can be collected upstream of the scrubbers and ash-free wastes can be produced. Concurrently, plans are being made to expand the disposal project to include two new impoundments for the evaluation of disposal of the gypsum, and the

ash-free waste that is dewatered, mixed, and compacted at the disposal site with low-moisture-content fly ash. Linings and underdrainage are being considered. These sites should be operating by the summer of 1976. Later in this project, one or two of the four untreated disposal areas will be drained of water and air dried. These sites will then be capped with a clay cover that will be contoured to drain rainwater and planted with vegetation. Monitoring will be continued for the quantity and characteristics of the leachate and for strength of the materials throughout the remainder of the project.

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METRIC CONVERSION TABLE

EPA policy is to express all measurements in metric units; however, for clarity, British units have been used in most instances in this paper. A list of conversion factors for the British units used is as follows:

<u>British</u>	<u>Metric</u>
1 acre	4047 m ²
1 ft	0.3048 m
1 g/ft ²	10.76 g/m ²
1 in.	2.54 cm
1 lb	453.6 g
1 mi	1.609 km
1 ppm	1 mg/l (equiv.)
1 psi	0.0703 kg/cm ²
1 ton (short)	0.9072 metric tons
1 ton/ft ²	9765 kg/m ²
1 yd ³	0.7641 m ³

CHEMICAL FIXATION OF FGD SLUDGES -
PHYSICAL AND CHEMICAL PROPERTIES

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ABSTRACT

Five FGD sludges arising from three types of scrubbers and two sulfur content coals were subjected to physical and chemical analysis. Testing included the raw sludges and materials produced by chemical fixation utilizing five processes. Physical analysis included determination of bulk density, porosity, permeability, and unconfined compressive strength. Results of the physical tests were inter-correlated, but highly dependent on the fixation process employed. Chemical testing consisted of leaching experiments for both the raw and fixed sludges, conductivity, and sulfate data were presented in this paper. Little dependence between the results of the chemical and the physical tests could be detected. Source of the sludge and initial sulfur content of the coal did have an effect on leaching and fixation performance. Pollutant migration rates may be compared between fixed and raw products based on leaching mechanisms proposed in this paper, and will probably be useful in disposal operation design.

CHEMICAL FIXATION
OF
FGD SLUDGES - PHYSICAL AND CHEMICAL PROPERTIES

INTRODUCTION

The removal of sulfur oxides from flue gases to meet air quality standards is usually accomplished by scrubbing with a fluid which absorbs the sulfur oxides from stack gases. These scrubbers may be classified by the nature of the absorbant (or precipitant) employed; lime, limestone, or double alkali. The predominance of the existing scrubbers are nonregenerable; that is, the absorbant is removed from the system after a certain contact period. The use of nonregenerable flue gas desulfurization (FGD) systems by definition results in a residue or sludge for disposal. The ultimate disposal of these residues is usually on land, and attention must be directed at the potential environmental impact of such an activity.

Land disposal of sludges or residues may result in an adverse environmental impact if pollutants migrate from the disposal sites at rates greater than those compatible with acceptable environmental quality. The principle endpoint of this migration is usually groundwater or surface water systems. The resultant pollution of these systems is not compatible with proper disposal procedures; consequently, procedures must be employed to reduce the rate of pollutant migration. The techniques commonly employed to accomplish this objective include site selection/operation, liners, chemical fixation, and a combination of the above.

Site selection is used to assess the suitability of a disposal site prior to the actual disposal operation. Factors included within this analysis are geology, hydrology, and soil properties which would favor reduced pollutant migration. Liners are utilized as a barrier between the disposal site and the environment, and reduce pollutant migration by preventing flow of leachates from the disposal site to the surrounding environment. Chemical fixation is a process which alters the physical and chemical properties of the sludges to retard pollutant migration.

The U. S. Army Engineer Waterways Experiment Station is presently studying the chemical fixation of hazardous wastes and FGD sludges. The principle objective of this study is to assess the technical feasibility of chemical fixation and to specifically evaluate it based on physical and leaching tests. This paper will be confined to discussing the current results of the testing program for FGD sludges regarding the above tests. Discussion of the leaching test will be restricted to those data from conductivity and sulfate analyses. Properties of the sludges and their fixed products will be related to source of coal, and scrubber type.

METHODS

Sources of Sludges

The FGD sludges selected for the chemical fixation testing program are listed in Table 1. Included within Table 1 are the scrubber type, source of coal, sulfur content of the coal, and a code number associated with each sludge tested. All sludges originated from stationary power plants and were collected at the point prior to disposal at the respective sites.

Sludge Fixation

Fixation of the sludges was performed at the Waterways Experiment Station by the processors selected for inclusion in this study. The fixation processes employed will be identified by a code letter and the fixed material will be identified by a code letter and a number indicating sludge source. The processes were not universally employed to all FGD sludge types, since the decision to fix a particular residue was made by the individual processors.

Physical Testing

The physical test results included in this paper are for bulk density, porosity, permeability, and unconfined compressive strength. With the exception of the permeability test, all methods conform to those of the American Society for Testing and Materials (ASTM¹). Permeability of the raw sludges was determined by use of a falling head permeameter and by use of a triaxial testing machine for the fixed residues.

Leach Testing

Leach testing was performed on the raw sludges and fixed materials. The methods for leach testing have been documented in earlier project reports^{2,3}. All leach testing was performed in triplicate and utilized two leaching solutions of differing pH (4.7 and 7.7). The leachates were analyzed for specific conductance and sulfate by procedures presented in Standard Methods⁴.

RESULTS

The results for the physical testing of raw and fixed FGD sludges are presented in Table 2. Fixation of the FGD sludges results in a consolidated material which is generally of higher density, lower porosity and permeability, and demonstrates some degree of structural strength. These results are generally confirmed by the physical testing for processes A, E, and F. The results for processes B and G tend towards

Table 1 FGD SLUDGE DESCRIPTION

<u>Code Number</u>	<u>Coal Source</u>	<u>Percent Sulfur*</u>	<u>Scrubber Type</u>
100	Eastern	1.67	Lime
400	Eastern	1.82	Limestone
500	Eastern	2.00	Double Alkali
600	Western	0.60	Limestone
1000	Western	0.46	Double Alkali

*Based on coal analysis at the time of sludge sample collectio .

Table 2 PHYSICAL PROPERTIES OF RAW AND FIXED FGD SLUDGES

Sample ID	Bulk Density (lb/cf)	Porosity	Permeability (cm/sec)	Unconfined Compressive Strength (psi)
R-100	51.7	67.3	1.070×10^{-5}	-
R-400	63.1	64.2	7.784×10^{-5}	-
R-500	52.3	74.0	2.505×10^{-5}	-
R-600	89.0	48.5	1.439×10^{-5}	-
R-1000	47.4	75.4	6.536×10^{-5}	-
A-100	100.1	51.4	2.06×10^{-6}	100.3
A-400	108.3	55.6	-	-
A-500	95.5	57.8	1.13×10^{-7}	188.3
A-600	109.3	41.0	4.31×10^{-7}	403.1
A-1000	96.6	51.4	8.95×10^{-7}	337.4
B-100	77.0	75.3	1.59×10^{-4}	23.7
B-400	89.0	75.5	1.08×10^{-5}	44.5
B-500	90.8	71.6	4.56×10^{-5}	42.7
B-600	79.6	76.3	3.96×10^{-5}	35.3
B-1000	81.5	73.2	6.62×10^{-5}	23.2
E-100	101.1	45.7	7.94×10^{-4}	2570.0
E-400	82.7	55.4	2.52×10^{-6}	720.0
E-500	99.3	49.0	4.54×10^{-11}	2220.0
E-600	110.9	35.4	3.57×10^{-8}	4486.0
E-1000	82.7	50.8	7.33×10^{-7}	1374.0
F-100	-	-	-	-
F-600	81.0	52.4	5.01×10^{-6}	395.6
G-100	-	-	-	-
G-400	62.7	69.7	5.24×10^{-5}	242.6
G-500	52.5	75.4	1.39×10^{-4}	86.4
G-600	56.9	73.4	1.22×10^{-4}	126.1
G-1000	68.1	70.0	4.05×10^{-5}	144.3

the opposite of above, fixation resulting in a more porous material with higher permeability and lower structural strength. The physical properties appear to be dependent on a specific fixation process and are consistent with that process.

The results of the leaching tests for conductivity are presented in Figures 1-5, respectively. These data, as well as those for sulfate, will be grouped according to FGD sludge type. The results presented are for the acidic leaching solution and represent the mean for triplicate tests. A comparison of leachate properties as a function of leach solution pH for a hazardous waste has been presented previously⁵, and demonstrated that leachate properties are roughly independent of leaching solution pH for the range tested. These results appear to hold in a likewise manner for the FGD sludges and their fixed products. The conductivities for the leachates from the fixed material are generally equivalent to, or greater than, those of the raw sludges. An exception to this appears for sludge 500 in which the raw sludge leachate conductivity is significantly higher than the fixed materials. The trends for the conductivity data appear to follow a classical leaching phenomenon, a high initial concentration followed by a gradual decrease to a steady-state condition. This trend appears to be more evident for the double alkali scrubber sludges, and is particularly noticeable for residue 1000.

Historically, specific conductance has been used as a measure of dissolved solids present in a solution. This relationship is dependent on the chemical composition of any particular solution and should ideally be confirmed for a group of solutions. The results presented in Figure 6 are paired data for conductivity and dissolved solids on elutriates from all raw and fixed sludges utilized in this study. These data demonstrate a strong linear relationship between these parameters. This result may be used to interpret conductivity data derived from the leaching experiments by inferring a relationship to dissolved solids. Utilizing the relationship previously defined and the specific chemical analyses, a speciation of chemical form as well as an appropriate check of analytical methods may be made.

The results for sulfate are grouped in a similar fashion to those of conductivity and are presented in Figures 7-11, respectively. The leaching data for sulfate appear to be well correlated with conductivity and follow similar trends. The rapid decline in leachate sulfate concentration is more apparent for the double alkali sludges as compared to a relatively constant sulfate concentration for leachates from the remaining sludges. In the case of the double alkali sludges the leachates from the fixed materials are generally of superior quality than those from the raw

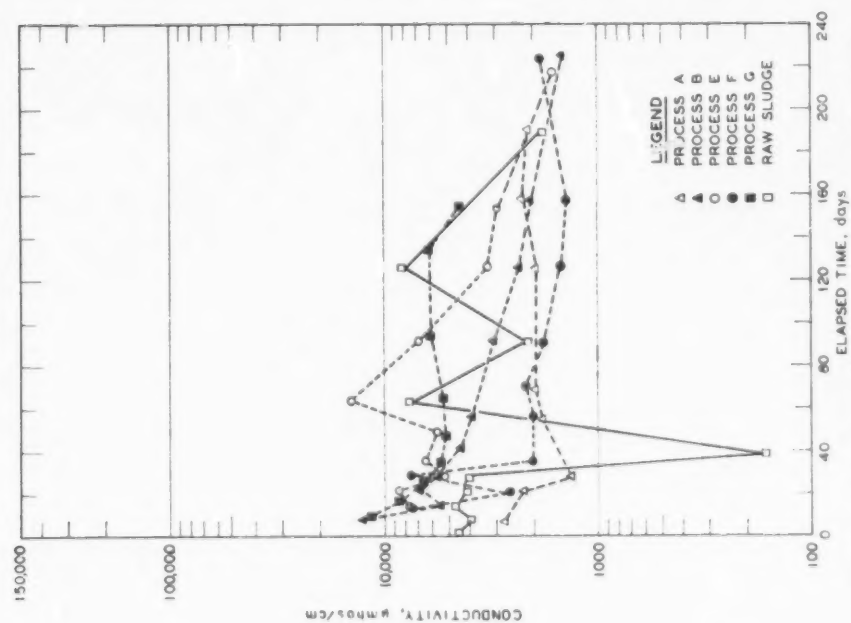


Figure 1 Leaching results, conductivity, sludge no. 100.

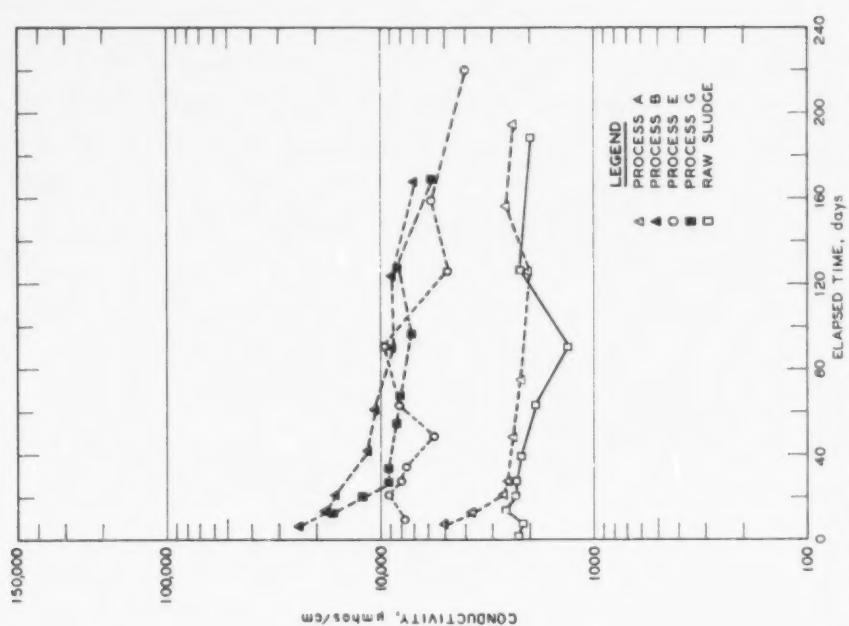


Figure 2 Leaching results, conductivity sludge no. 400.

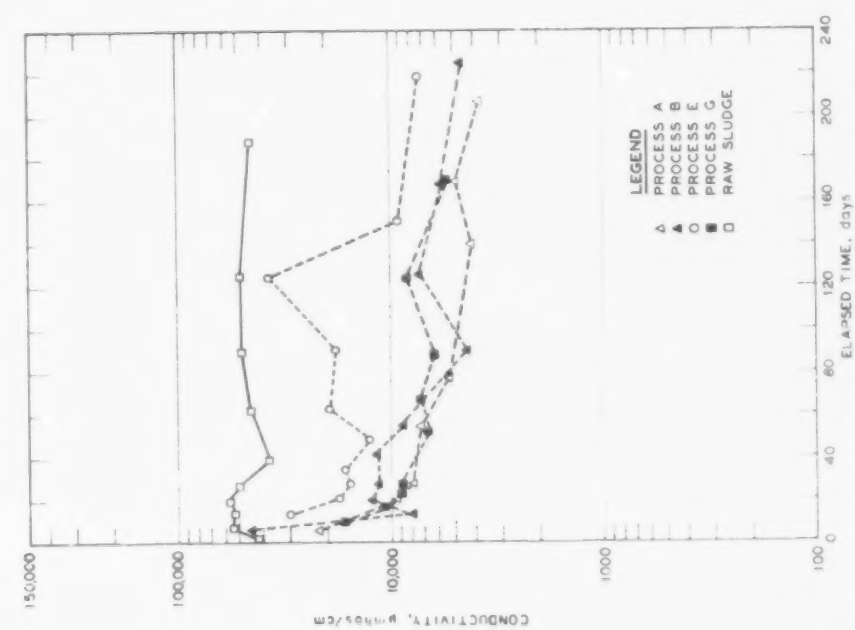


Figure 3 Leaching results, conductivity, sludge no. 500.

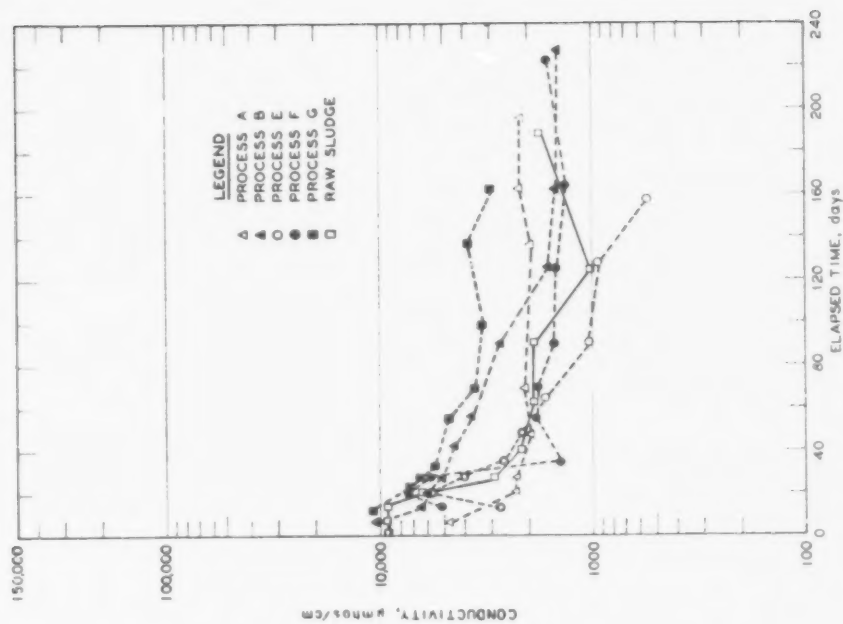


Figure 4 Leaching results, conductivity, sludge no. 600.

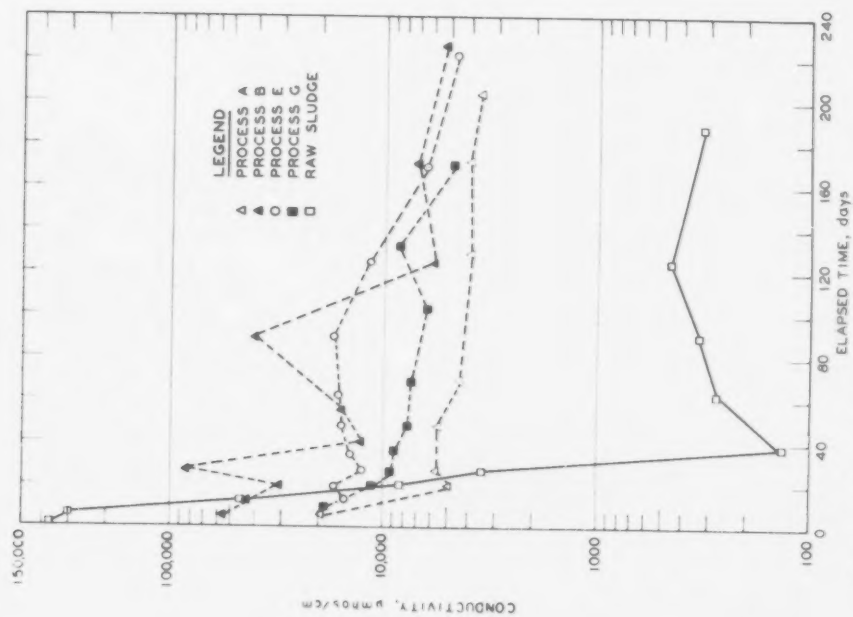


Figure 5 Leaching results, conductivity, sludge no. 1000.

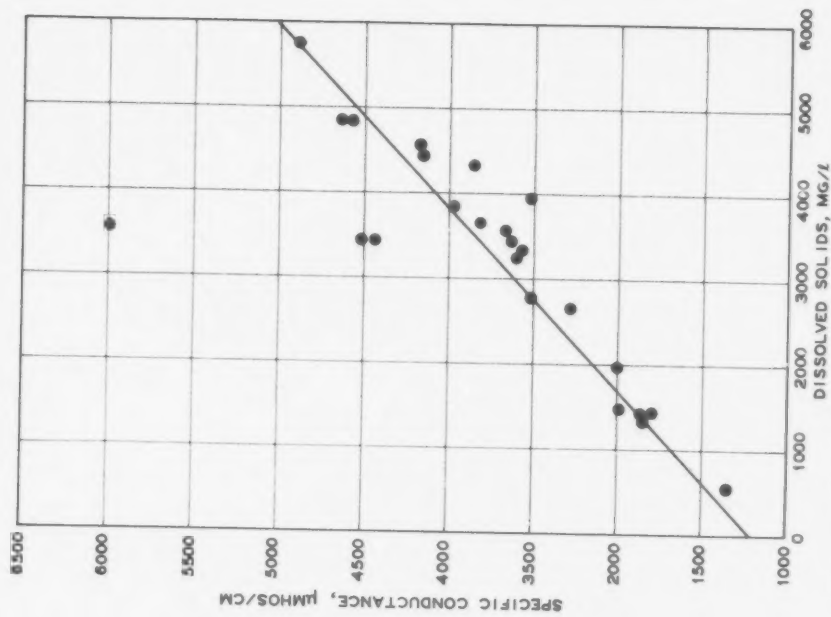


Figure 6 Conductivity vs. dissolved solids.

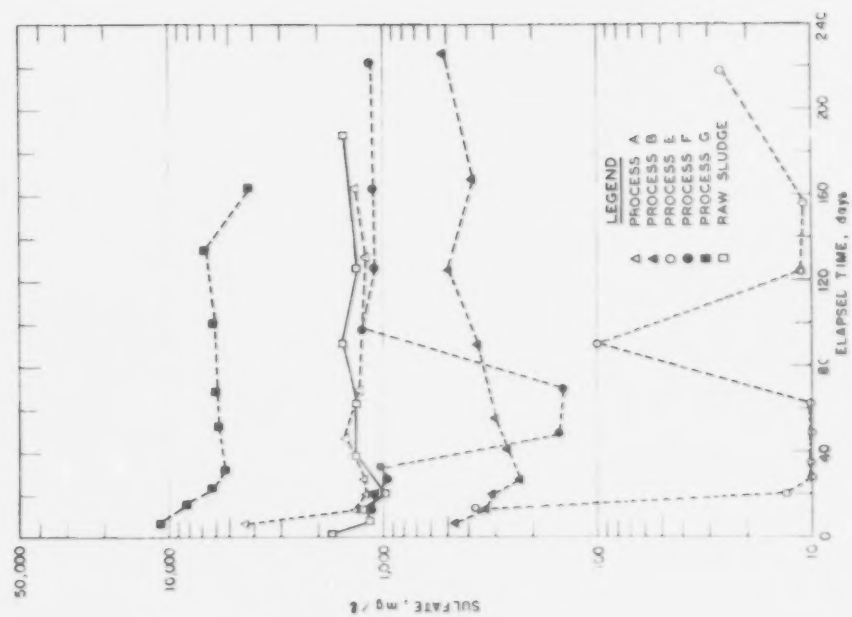


Figure 7 Leaching results, sulfate, sludge no. 100.

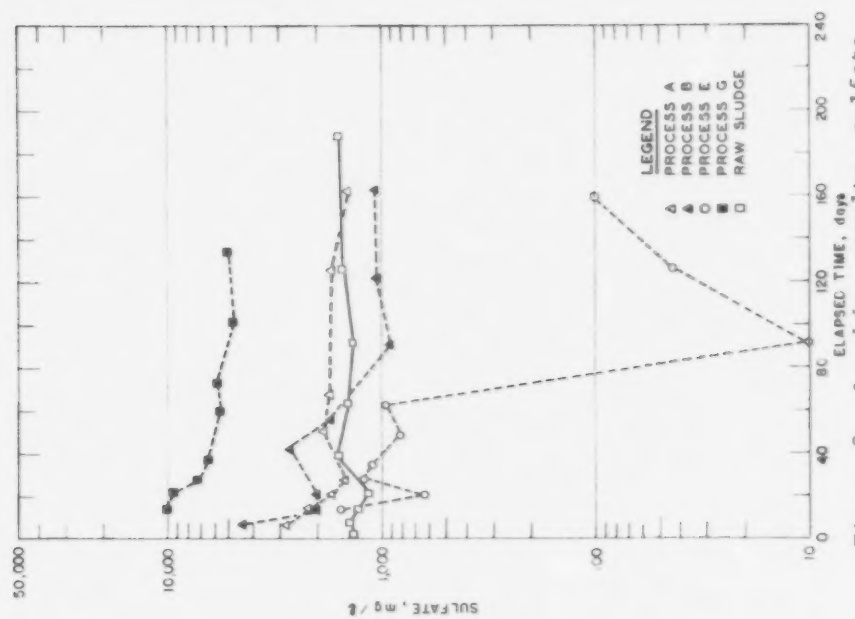


Figure 8 Leaching results, sulfate, sludge no. 400.

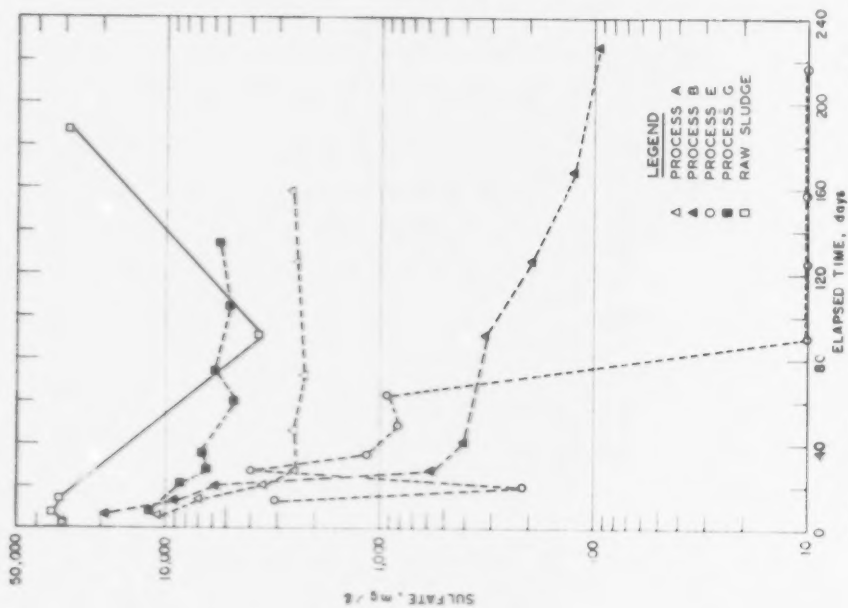


Figure 9 Leaching results, sulfate, sludge no. 500.

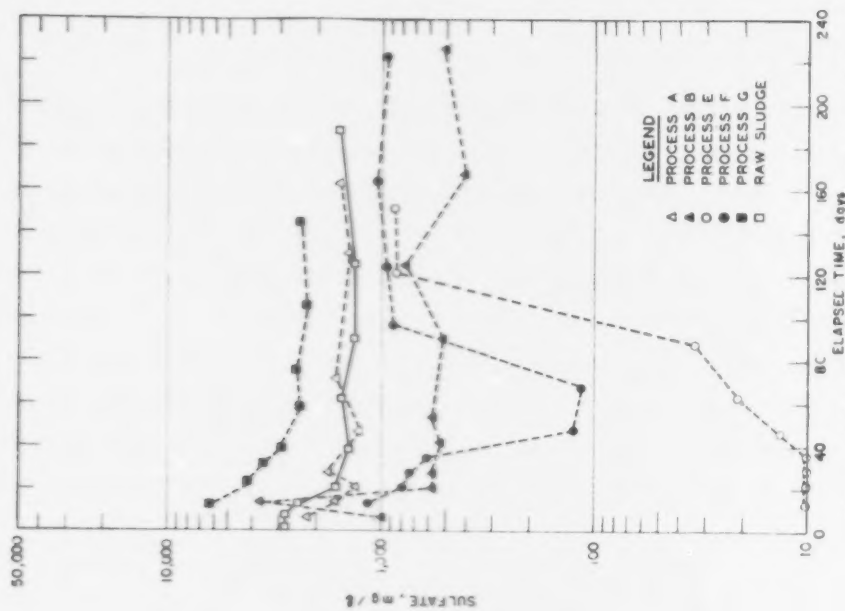


Figure 10 Leaching results, sulfate, sludge no. 600.

sludges. In contrast, the remaining sludges demonstrate an equivalent quality between fixed and raw sludges and a significant presence of sulfates in all leachates.

DISCUSSION OF RESULTS

One principle result of residue fixation is generally an alteration in the physical properties of the material. These alterations are manifested by a consolidation of the sludge into an agglomerate mass which demonstrates a certain structural strength. From a material behavior with respect to leaching, the consolidation of residue material will be reflected in a transition from a solubility mechanism to a diffusion mechanism for pollutant migration. These mechanisms will realistically reflect field conditions if the permeability of the fixed material is significantly less than that of the surrounding material in which the fixed material is placed. Initially, both materials will exhibit similar leaching behavior until surface wash-off from the fixed materials has occurred and the diffusion mechanism becomes dominant.

The conductivity data for the FGD sludges appear to support the above observations. Leachates from the raw sludge are generally characterized by a constant conductivity. Sludge 1000 demonstrated a rapid decline in conductivity to a stable level. This would indicate a transition between quantities and types of chemical forms available for solubilization within this material. The fixed residues demonstrate an initial decline in leachate conductivity with a subsequent stabilization in quality indicating the predominance of the diffusion mechanism.

It may be generally postulated that there is a relationship between physical properties of a fixed material and the leachate quality produced. This relationship will hold if there exists a link between physical properties of a fixed material and the diffusion mechanism which characterizes leaching. This observation must be qualified for a specific fixation process. Chemical alterations which affect leaching behavior may not necessarily be reflected in the physical properties of the material. To investigate this relationship a plot of unconfined compressive strength versus relative leachate sulfate concentration is presented in Figure 12. There appears to be no relationship between specimen strength and leachate quality for the fixed FGD sludges. An increase in structural strength is related to decreased sulfate concentrations in the leachates but appears to represent a lower bound for sulfate leaching. It may be concluded from these data that alteration in physical characteristics of the FGD sludges will increase leachate quality after a

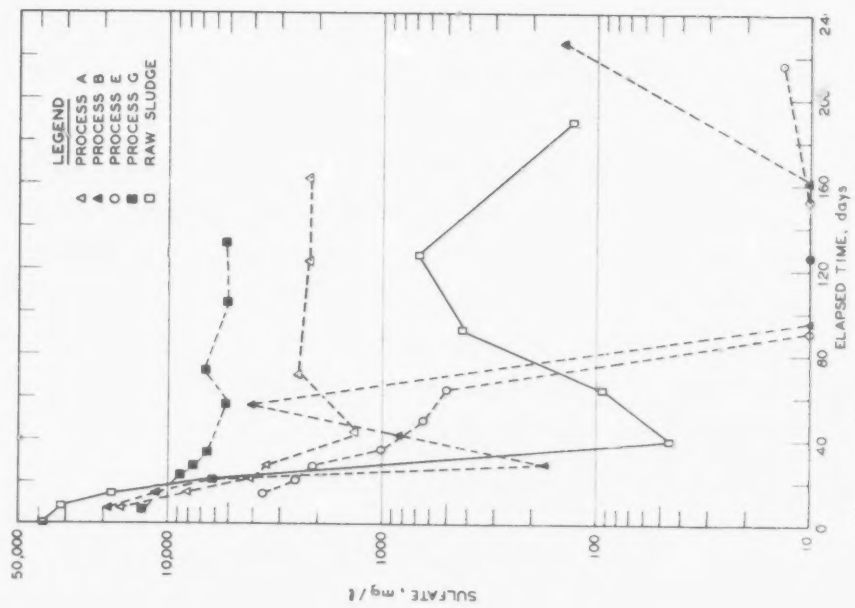


Figure 11 Leaching results, sulfate, sludge no. 1000.

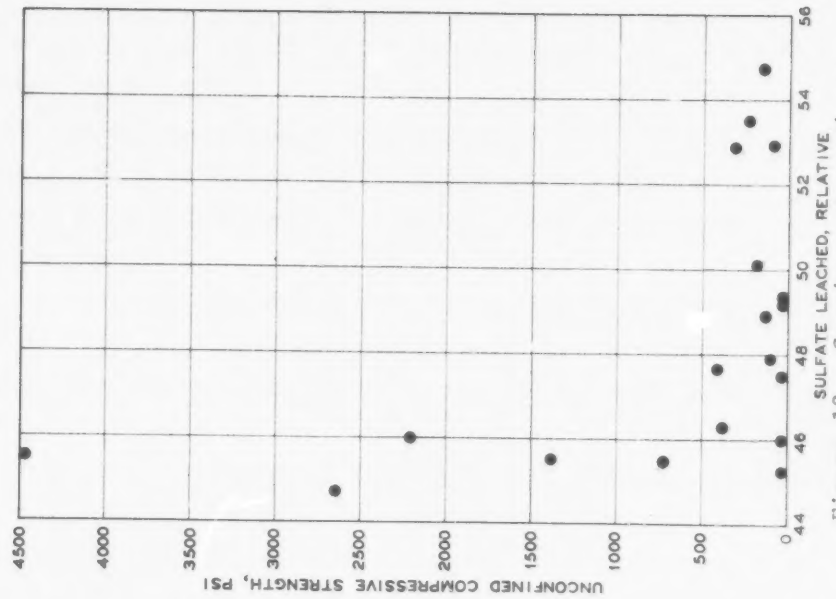


Figure 12 Specimen strength vs. sulfate leaching.

certain degree of modification is obtained. The remainder of the variation of sulfate quality for the leachates must be attributed to chemical modification in fixed materials.

The selection of FGD sludge samples within this effort presents an excellent opportunity to evaluate fixation performance as a function of sludge category. To accomplish this analysis, the sulfate data from the limestone and double alkali scrubbers for eastern and western coals and for processes A, B, E, and G were analyzed. The procedure used for analysis involved canonical decomposition of the data followed by graphical presentation of the results. A similar technique has been used previously for the analysis of water quality data⁶. The results of the analysis for double alkali scrubbers is presented in Figure 13. The horizontal bars representing sulfate leaching for the raw and fixed products are proportional to the 5 percent confidence limits for the data, and distances between bars represent differences between groups. This presentation is analogous to an analysis of variance which is based on within and between group variation. The scale is relative, but comparisons may be made between fixed and raw groups by noting that displacement to the right indicates increasing sulfate leaching and displacement to the left, the converse. The analysis is presented by coal origin which is related to initial sulfur content, Table 1. It is interesting to note that the data for one scrubber type (e.g., limestone or double alkali) were well correlated between scrubber type. This result would tend to indicate that leaching of raw and fixed materials (or sludges) is very dependent on the scrubber source, and this factor may play a critical role in disposal.

The results of this statistical analysis for double alkali scrubber sludges is presented in Figure 13. In this case a dramatic improvement in leachate quality may be noted for both coal origins. This fact is related to the fixation process and agglomeration of the residue to reduce the availability of the more soluble sodium sulfate present in these sludges. The performance of all fixation processes appears to be roughly equivalent and does not demonstrate the variability shown for the limestone scrubber sludges, Figure 14.

A similar analysis for the limestone scrubbers, Figure 14, demonstrates a significant effect of coal origin on the performance of fixation. The fixed materials originating from the eastern coal scrubber show a deterioration in leachate quality for sulfate, while fixed materials for western coals show a slight improvement. Examination of the sulfate data, Figures 8 and 10, would confirm this statement.

LEACHATE QUALITY

DOUBLE ALKALI SCRUBBER

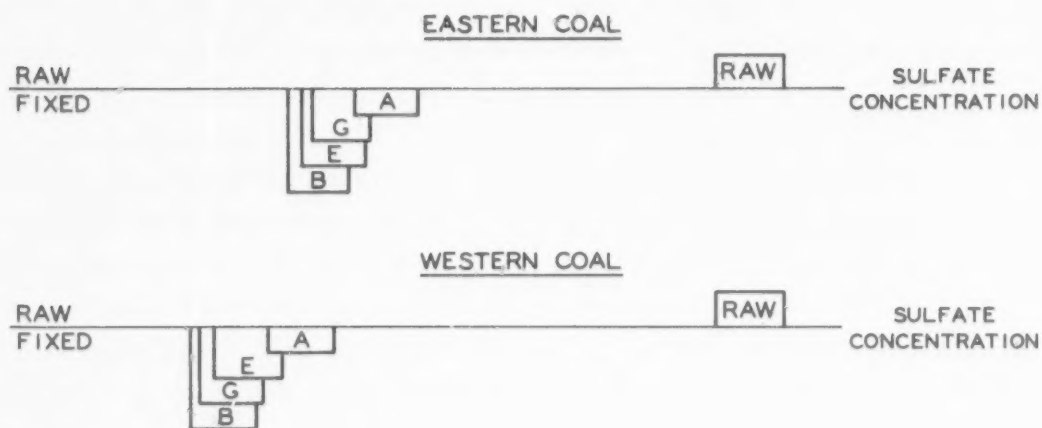


Figure 13 Fixation performance, double alkali scrubber sludges.

LEACHATE QUALITY

LIMESTONE SCRUBBER

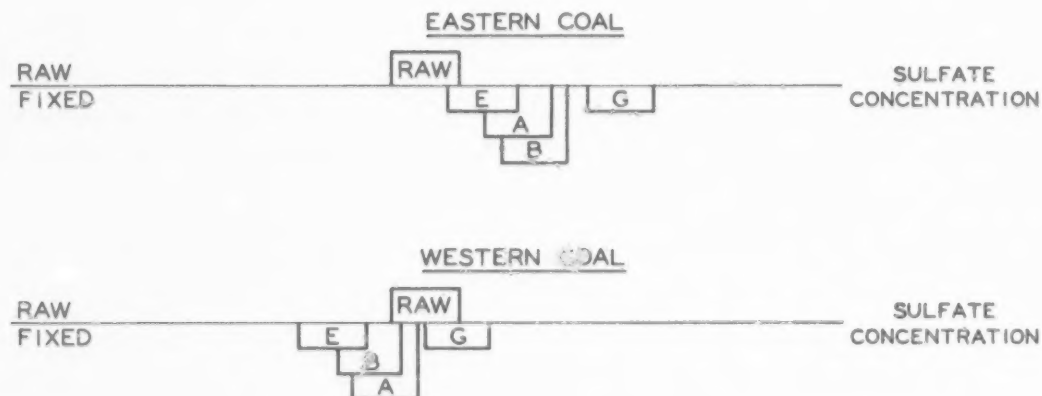


Figure 14 Fixation performance, limestone scrubber sludges.

The sulfate leaching from these samples, Figures 8 and 10, appears to be at the solubility of calcium sulfate and differences between fixed materials may be a function of sulfate availability between the two types of sludge.

It may be concluded from this analysis that the leaching and performance of fixed FGD sludges is strongly dependent on the type of scrubber and, for the limestone scrubbers, is dependent on the source of coal (initial sulfur content). The double alkali scrubbers tend to produce more soluble sulfate compounds and thus their leaching behavior is affected by fixation to a greater degree. The limestone scrubbers produce less soluble sulfate compounds and fixation of these sludges affects the leaching of sulfate to a minor degree. Within the limestone scrubber sludges, the amount of sulfate available appears to be proportional to the initial sulfur content of the coal utilized. The western coals, which have a lower sulfur content, produce less available sulfate in the sludge and the fixed materials demonstrate an improvement in leachate quality. The limestone scrubber sludges from eastern coals have sufficient available sulfate such that agglomeration (fixation) of this residue does not affect the leaching behavior of the material.

The interpretation of leaching data based on laboratory experiments must be qualified to some degree by accounting for conditions which exist at a field disposal site. The leaching of the raw FGD sludges is primarily a function of the solubility of the pollutants present within the sludge. The fixed materials, because of their agglomerate nature, leach primarily via a diffusion mechanism after initial wash-off of surface bound pollutants has been attained. The performance of the fixed materials in an actual disposal site is related to the available surface area subject to leaching and ultimately to the stability of the agglomerate in the field. An extrapolation of laboratory leaching tests to field conditions has been made for hazardous wastes⁵, and the data show a significant improvement in leachate quality after fixation of the sludge.

The stability of a fixed material in a field disposal site is related to its durability and resistance to degradation. Destruction of the agglomerate will increase the effective surface area which is subject to leaching and subsequently increase pollutant migration rate. To test the effect of these parameters on the leachability of a field disposal site an analysis was made based on the following assumptions:

- (a) Pollutant migration from a raw sludge disposal site (Volume = 1000 m^3 , depth = 3 m) is a function of pollutant solubility and permeability of the sludge material.

- (b) Pollutant migration from a fixed sludge disposal site (Volume = 1000 m^3 , depth = 3 m) is a function of initial pollutant present (assumed to be 10^5 mg) and the effective diffusivity⁷.

The results of this analysis are summarized in Figure 15. Pollutant migration from a raw sludge disposal site is presented in a family of curves covering a permeability range from 1×10^{-3} to $1 \times 10^{-5} \text{ cm/sec}$. Pollutant migration from a fixed sludge disposal site is presented as a family of curves for effective diffusivities ranging from 1×10^{-9} to $1 \times 10^{-11} \text{ cm/sec}$. The curves are parallel indicating that equivalent conditions between the two leaching mechanisms will give similar pollutant migration rates. Given a leaching condition for a raw sludge and the effective diffusivity for a fixed material, both of which may be experimentally determined, an upper bound for effective surface area may be established. An increasing effective surface area is synonymous with agglomerate destruction and can be estimated from the properties of the fixed material.

The increase of effective surface area by a fixed material does have a bound at which time the leaching mechanism will become solubility limited but not diffusion limited. This transition probably would occur when the effective surface area exceeds 100. The lower bound on effective surface area is theoretically zero, but a practical limit of 0.1 has been assumed. The foregoing analysis is dependent on the type of pollutant considered and will vary depending on interactions with chemical or biological mechanisms affecting pollutant migration. Determination of the effective diffusivity may be made on certain specimen sizes and is assumed to hold over a reasonable range. Chemical effects of fixation may alter the diffusivity as a function of effective surface area and possibly will introduce an error into the analysis. The above presentation will allow comparison of fixed and raw sludge disposal operations, and knowing conditions of the site, may be used to select a required diffusivity for a fixed material. Alternately, the analysis may be coupled to soil movement and attenuation factors plus groundwater hydrology to give an estimate of environmental impact for selected disposal methodology.

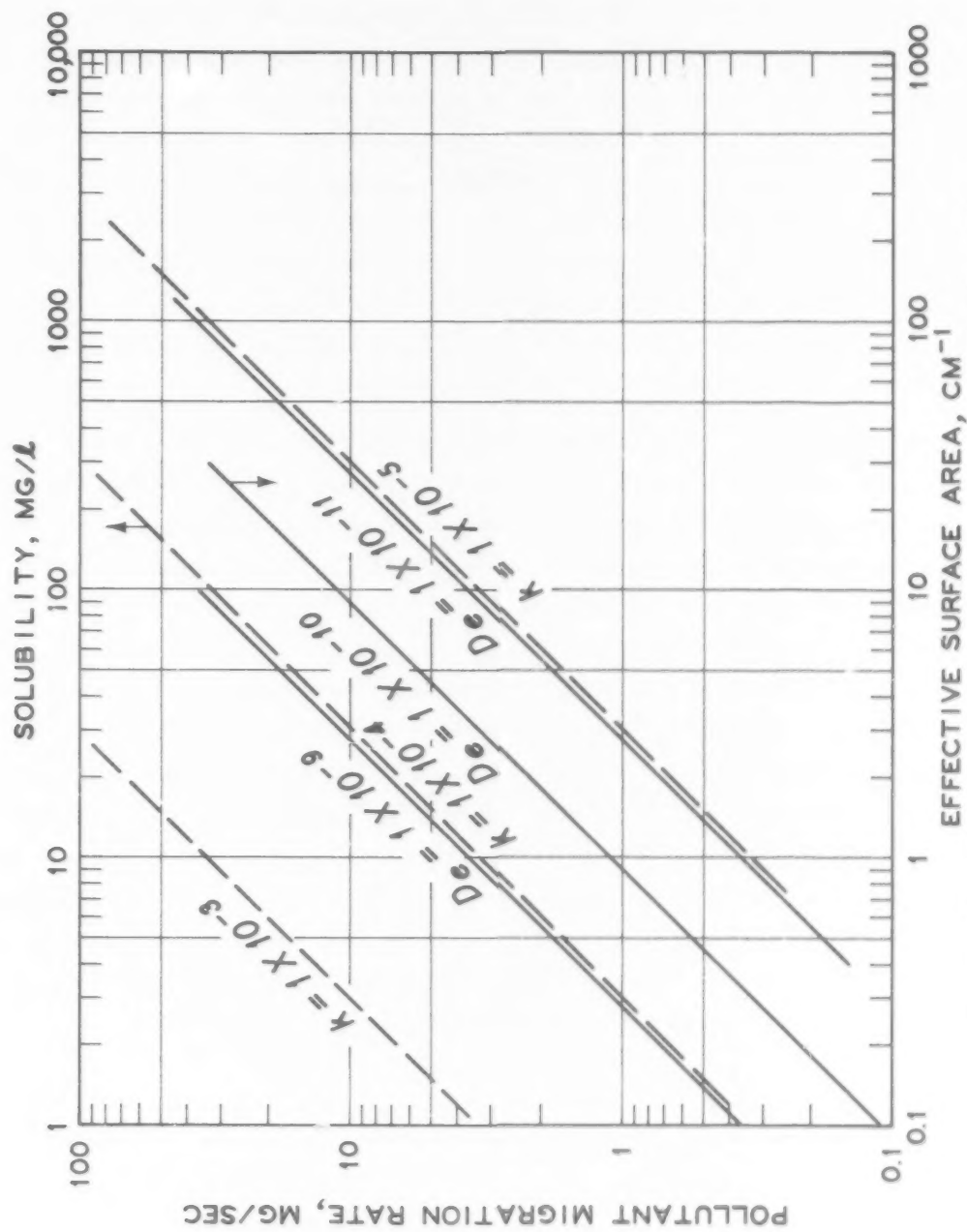


Figure 15 Disposal impact, sulfate, raw and fixed FGD sludges.

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POTENTIAL UTILIZATION OF CONTROLLED SO EMISSIONS
FROM POWER PLANTS IN EASTERN UNITED STATES

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ABSTRACT

This EPA sponsored study (EPA-IAG-D4-0500) was initiated to evaluate the potential marketing of abatement acid and sulfur from fossil-fuel-fired power plant sources in eastern U. S. A systems approach was selected to manage the data bases needed to identify the social cost associated with the alternative choices for reducing SO emissions in our market-oriented economy. Although conclusions will not be published until data bases and State Implementation Plans have been further refined and verified, several intermediate results are worth noting. A possible Frasch sulfur shortage in the next ten to twenty years was identified. Since sulfur is a vital resource in the American economy, every effort should be made to recycle it into productive use.

Total potential abatement production from 2,564 boilers in eastern U. S. (22.3 million tons of 100% acid) could have been absorbed in the existing market. However, the by-product market simulation model derived for this study demonstrated in the first case that at zero incentive cost, there would be no significant abatement production at power plants. But as power plants are forced to reduce emissions, the cost of alternative controls can be a credit to recovery processes and thereby provide a basis for assigning a market adjustment value. At the highest level of market adjustment analyzed, \$65/ton H_2SO_4 (23¢/million Btu), 38 boilers produced 3.3 million tons in the equilibrium solution. This represents a total market adjustment of \$214 million/yr (about 2.5 mills/kWh). Seventy-one million of this can be identified in the model as savings to the utilities (producer surplus) and acid industry (consumer surplus). Hence the real cost to society is only \$143 million to control 65% of the excess SO_2 emission problem. Society would gain, however, which is not the case with a throwaway strategy.

A second case analyzed the throwaway sludge alternative assuming that marketing revenue would have to exceed the cost differential before acid production would be selected. Considering all boilers (169) with cost less than \$175/ton of H_2SO_4 (61¢/million Btu), scrubbing in competition with acid produced from \$60/ton sulfur, 7.4 million tons (152 boilers) of abatement acid (96% of total considered) could be produced in lieu of throwaway sludge.

Conclusions thus far must be tempered with possible clean-fuel market developments, future sulfur price levels, air pollution regulations, and further verification and refinement of the data bases.

POTENTIAL UTILIZATION OF CONTROLLED SO_x EMISSIONS

FROM POWER PLANTS IN EASTERN UNITED STATES

INTRODUCTION

A noted economist, Dr. Kenneth Boulding, suggests we move from a throughput economy to the concept of spaceship earth. He infers that our economic survival and comfort in the long run may depend on our ability to recycle our waste products in a way that assures continual replenishment of the raw material base. This concept agrees with the fundamental physical law of the conservation of mass. That is, every ton of material removed from the earth and transferred into goods still remains to be disposed of when the goods in question are finally consumed. Society has the choice of either disposing of the waste products in an acceptable manner or recycling the abatement materials into productive use. This EPA sponsored study attempts to identify the social cost associated with the alternative choices for managing the SO_x emissions from fossil-fuel-fired power plants in our market-oriented economy.

The first phase of this work was reported at the last Flue Gas Desulfurization Symposium (FGD), Atlanta, Georgia, November 1974.¹ The study focused on the TVA power system as an example of theoretical production and distribution of abatement sulfuric acid. Although hypothetical, it provided insight as to the impact that abatement sulfuric acid could have on the existing market.²

Phase II involved a preliminary market study of the potential use of calcium-sulfate sludge by the wallboard fabrication industry. This too was reported at the last FGD symposium.³

The current phase of this work, identified as Phase III, expands the first phase to include elemental sulfur as well as sulfuric acid as a potential byproduct from the FGD processes installed in power plants located in the states served by the inland waterway system in eastern U.S. The objectives were outlined to provide general and practical information concerning the current production, distribution, and use of sulfur and sulfuric acid in the U.S. The computer programming model of Phase I was expanded to cover the power plant data base and programmed to reflect pollution restrictions established by State Implementation Plans (SIP). The model was designed for multiproduct capability and ease of modification to accommodate the expanded data bases.

As the data bases were acquired, verified, adapted, and cataloged, it became apparent that available information was adequate to assess all power plant and acid plant candidates in the U.S. Also, the recent influence of smelters and sour gas sulfur sources on the

Frasch sulfur market is reaching a point (25%) that cannot be ignored. The need for increasing the accuracy of the cost screen for FGD systems by use of a retrofit difficulty factor also became apparent. Complexity of the model was so great that additional refinement was also desirable. Due to these considerations, it was decided that an interim report describing progress to date, design of model, and possible uses would be in order, and a final report would be prepared later covering full assessment of markets for abatement sulfur and acid from all sources in the 48 contiguous states of the U.S.

Phase III Interim Report

As the work progressed on this project, unique research opportunities became apparent. The 1972 Federal Power Commission (FPC) Form 67 data file contained power plant operating variables which matched the detailed cost estimates of the five leading FGD processes prepared by TVA in January 1975 (EPA 600/2-75-006).⁴ Availability of these data presented the opportunity to develop a cost screen designed to focus on the most promising power plant boiler candidates for abatement byproduct production. It was also learned that the 1973 FPC Form 67 data, which would not be available until late 1975 or early 1976, would contain 5- and 10-yr projections of proposed new power plant installations. SIP standards for air pollution control effective in March 1975 identified allowable emissions for each power plant in the U.S. A Rail Transportation Rate Generation model being developed by TVA had reached the point that with concerted effort, accurate transportation rates for elemental sulfur and sulfuric acid could be generated in this system for all origins and destinations in the rail rate territories located east of the transcontinental territory. To take advantage of these opportunities, the project was expanded to provide a more meaningful research effort.

A systems approach was selected to combine data inputs needed to expand the scope of study, refine the data bases, impose emission restrictions, and accurately assess the nationwide market potential for abatement byproducts. Five major data bases -- for (1) sulfuric acid producers, (2) transportation-distribution options, (3) steam plant boilers, (4) SIP data, and (5) TVA cost estimate data -- feed a market simulation model through three cost generation modules. Estimated long-run competitive equilibrium solutions based on realistic outputs of abatement byproducts are achieved.

A flow diagram of the major system design requirements is shown in Figure 1. As part of the model design, it is assumed that the sulfuric acid market can be simulated as though all consumption occurred at sulfuric acid plants, and that acid-producing firms would close these plants and buy abatement acid if acid prices were below their

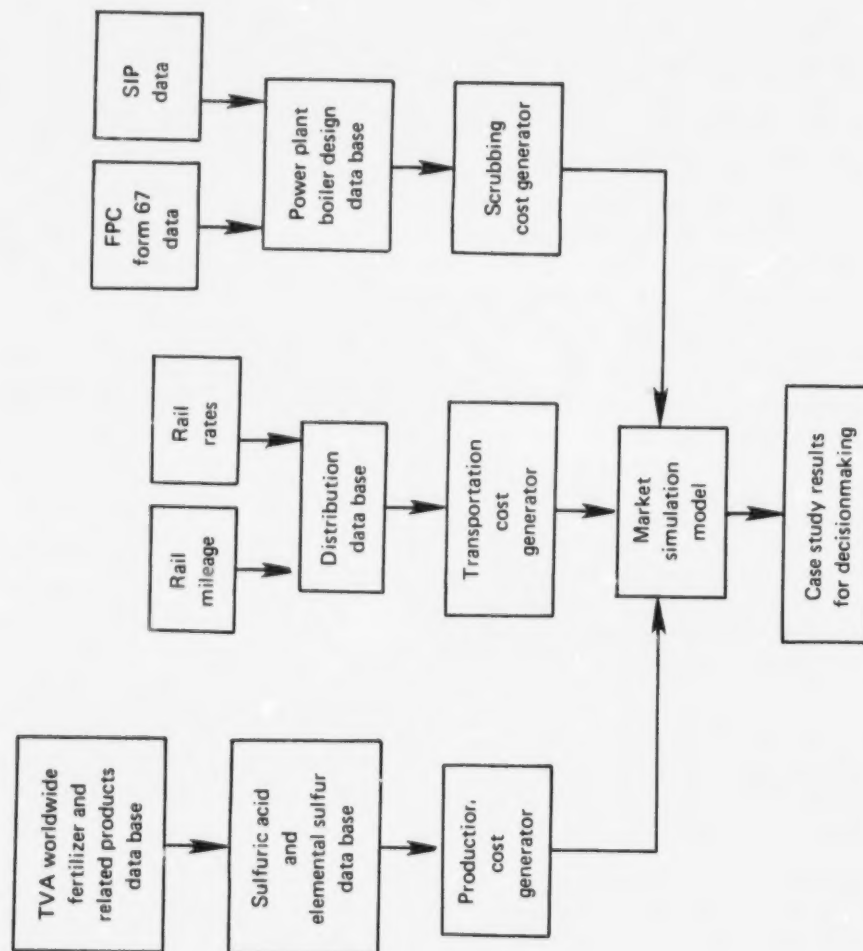


Figure 1. Flow diagram for major system design requirements

expected long-run average total cost. It is also assumed that steam plants would produce sulfuric acid or sulfur if that were the least costly (after credit for sales income) alternative for meeting clean air requirements. Given these conditions, it is believed that long-run competitive equilibrium market conditions can be simulated by minimizing the cost to both the sulfuric acid and power industries. In this framework, power plants are assumed free to produce or not produce sulfur or sulfuric acid and to sell to any sulfuric acid plant in competition with other power plants. Likewise, the sulfuric acid plants are assumed free to continue buying sulfur from traditional sources or from power plants, and free to buy acid in lieu of production subject to competition in their respective industries. Product differentiation is not assumed significant. Problems of stable, guaranteed abatement supplies are ignored, but probably are solvable. Rail transportation cost is assumed adequate for simulating competitive market conditions, though barge-truck strategies could be considered in some cases as more refined data analyses are made.

Model Complexity and Scope

As a methodological consideration, the computer model designed is directed toward identifying major candidates for abatement byproduct production and consumption.

From a data bank maintained at the TVA National Fertilizer Development Center, design and operating inputs were cataloged in the computer for existing U.S. contact process sulfuric acid plants. Capital and operating costs for mining sulfur by the Frasch process, marketing terminal storage, manufacturing acid by the contact process with storage, and controlling acid plant tail gas emissions were calculated to determine the competitive costs of sulfur and acid production.

An extremely important component of the model is the transportation data base for computing accurate shipping costs for sulfur and acid. Since shipping cost is an essential element in the price of acid and sulfur, a great deal of creative and complex effort was required to derive usable values for the entire U.S.

By the use of power plant design and operating data provided in the FPC Form 67, a data bank was constructed to accommodate key operation parameters for all power plants in the U.S. For this effort, only boilers burning coal or oil are of interest. Parameters such as fuel type, sulfur in fuel, boiler heat rate, fuel consumed, on-stream time, age of plant, etc., are vital. Using these data, possible output of byproducts can be calculated for each power plant -- given the level of SO₂ control designated by March 1975 SIP standards.

THE EXISTING FRASCH SULFUR INDUSTRY

Most of the sulfur consumed in the U.S. is used to produce sulfuric acid which in turn is mostly used in the manufacture of fertilizers. Sulfur is also used to produce such items as carbon disulfide, pulp and paper, insecticides, specialty steels, and leather goods. A breakdown of the estimated domestic consumption of sulfur in 1975 is given in Table 1.

Table 1. CONSUMPTION OF SULFUR IN THE U.S.⁵

Use	1975 (estimated)	
	Amount (000's long tons)	% of total
Carbon disulfide	236	2.1
Pulp and paper	541	4.9
Rubber	39	0.4
Sulfur dioxide	59	0.5
Agriculture	89	0.8
Phosphorus pentasulfide	44	0.4
Other	<u>205</u>	<u>2.6</u>
Total nonacid	1,303	11.7
Acid	<u>9,839</u>	<u>88.3</u>
Total	11,142	100.0

Note: For metric system conversion factors see Appendix A.

Sulfur enters into the production of many products in varying amounts, ranging from 18.090 tons of sulfur or sulfur equivalent per ton of Uranium 235 to 0.0003 ton per ton of phenol-formaldehyde plastic molding compound. The amount of sulfur consumed per ton of manufactured product is shown in Table 2.

Frasch sulfur production is a mining operation. Wells are sunk into a sulfur-bearing stratum, sulfur is melted by hot water injected into the stratum, and the molten sulfur is pumped out. The molten sulfur is pumped from the well to either heated tanks for storage as a liquid or to vats where it cools and solidifies.

Domestic sulfur production in 1972 was 10.2 million long tons mostly from mines in Texas and Louisiana. This was 24% of the estimated

Table 2. TONS OF ELEMENTAL SULFUR OR EQUIVALENT ELEMENTAL SULFUR
REQUIRED IN MANUFACTURE OF ONE TON OF INDICATED PRODUCT

Product	Short tons of sulfur or equivalent sulfur per ton of product ^a	Equivalent tons of H ₂ SO ₄
Fertilizers		
Diammonium phosphate (DAP) 18-46-0 grade	0.443 ^b	1.355
Granular triple superphosphate (GTSP) 0-46-0 grade	0.311 ^b	0.951
P ₂ O ₅ in 54% P ₂ O ₅ wet phosphoric acid	0.943 ^b	2.885
Wet phosphoric acid (54% P ₂ O ₅)	0.509 ^b	1.557
Granulated ammonium polyphosphate (GAPP) 12-57-0	0.538 ^b	1.646
Normal superphosphate (NSP) 0-20-0 grade	0.121 ^b	0.370
Liquid fertilizer 11-37-0 grade	0.646 ^b	1.976
Sulfuric acid, 100%	0.338 ^c	1.000
Synthetic fiber intermediates		
Hydrogen cyanide (Modacrylic fiber)	0.081	0.248
Caprolactan (nylon 6 fiber)	1.019 ^d	3.117
Acetate rayon (fibers, photographic film, etc.)	0.034	0.104
Synthetic rubber (SBR)	0.005	0.015
Vulcanized synthetic rubber (SBR)	0.012	0.037
Carbon disulfide (fibers, cellophane, other chemicals)	0.936	2.863
Paper pulp	0.109	0.333
Indigo dye	0.297	0.909
Pheno-formaldehyde plastic moulding compound	0.0003	0.001
Phenol by sulfonation (plastics)	0.441	1.349
Explosives		
Nitrocellulose	0.169	0.517
Black powder	0.100	0.306
Nitroglycerine	0.014	0.043
Lithopone paint pigment	0.105	0.321
Leather tanning		
Vegetable tan	0.007	0.021
Chrome tan	0.076	0.232
Bordeau mixture (4-4-50) (fungicide)	0.002	0.006
Treflan (100%) (herbicide)	0.420	1.285
Alum, 17% Al ₂ O ₃ (water treatment chemical)	0.150	0.459
Sodium dichromate (tanning, dyeing, paint pigments, etc)	0.142	0.434
Uranium 235	18.090	55.341
Sodium sulfate (100%)	0.226 ^e	0.691
Ammonium sulfate (100%)	0.243 ^f	0.743

^aAll values are from Shreve, R.N. Chemical Process Industries 3rd Edition, McGraw-Hill Book Company, New York, 1967, unless otherwise noted.

^bUnpublished TVA data.

^cAverage of several published values.

^dAnon. Chemical Week, June 26, 1974, p. 41.

^eAssuming direct neutralization of sulfuric acid with sodium hydroxide with no losses.

^fAssuming direct neutralization of sulfuric acid with ammonium hydroxide with no losses.

world production of 43.0 million tons. The same year Frasch sulfur accounted for 72% of all domestic sulfur production. Recovered sulfur accounted for 19% of domestic production, byproduct sulfuric acid from smelters, 5%, and other sources, mainly pyrites, accounted for the balance, 4%. About 74% of the domestic Frasch sulfur production was for domestic consumption, 22% for export, and 4% for increases and adjustments in producers stocks.⁶

In 1972 the Frasch sulfur supply (7.29 million long tons) was produced by five companies operating 13 individual mines. The three major companies were Duval Corporation, Freeport Minerals Company, and Texas Gulf Incorporated. Operating 10 mines, they accounted for more than 90% of the Frasch production and more than 65% of domestic production of sulfur in all forms. The five largest mines owned by these companies produced 73% of the Frasch sulfur and 52% of the total domestic sulfur supply in all forms.

Field surveys conducted during this study revealed a unique characteristic of the Frasch sulfur mining process: The development of a sulfur dome can be compared to the punching of pins in a pin cushion. Each well punched into a sulfur dome formation has an expected life of 1-2 yr. At any time the sulfur mine can have several wells operating in parallel. The number of wells depends primarily on the short-run market demand. As the mining process for a given dome reaches the mature stage, operating costs increase at an increasing rate due to the increased water and energy requirements. This incremental increase causes the supply price of sulfur to rise to a point where it is no longer economical to continue mining the sulfur dome.

Sulfur can be marketed either in the liquid or dry solidified form. It is estimated that more than 95% of all domestic sulfur deliveries to acid plants are in liquid form. March 1975 list prices f.o.b. Port Sulphur, Louisiana, are about \$60/long ton.⁸

Most molten sulfur is shipped by water from the mines or transshipment terminals on the Texas and Louisiana Gulf Coast to the marketing terminals. The basing point for the Gulf Coast market is Port Sulphur. Marketing terminals are strategically located either on the inland waterway system or along the east coast adjacent to ports served by deep-water vessels. From the marketing terminal, molten sulfur is transported by barge, truck, or rail directly to the point of consumption. March 1975 transport rates were used in this study.⁹

The delivered cost of sulfur to each acid plant in the model is based on \$60/long ton for sulfur f.o.b. Port Sulphur plus transportation cost. The sulfur transportation costs used are based on water transportation from Port Sulphur through marketing terminals by either truck or rail to the acid plant, whichever is lower cost. Average

sulfur storage costs were established at \$1.35/long ton for the program model used to calculate the production cost of H_2SO_4 in this study. The least cost mode for transporting sulfur was extended to cover a relative comparison of rail transportation from Port Sulphur versus water transport - terminal throughput - truck or rail to the acid plant. This least cost mode was selected in all cases for sulfur delivered to a given acid plant.

The Long-Run Sulfur Supply in the U.S.

G.H.K. Pearce recently completed a study on the long-run sulfur supply for North America.¹⁰ He projects the long-run sulfur supply price gradually increasing from \$10 to \$40/ton f.o.b. mine in 1970 dollars (about \$50 in 1974). The resulting sulfur supply price increase will encourage the relatively inefficient Frasch and native sulfur mines to become producers over time. He projects that the current sulfur reserves in the U.S. from conventional sources (Frasch process, native ore, petroleum, natural gas, sulfide ores, and pyrite) in the amount of 290 million tons will be mined out at current production rates by 2000 A.D. During the same period it is estimated that 110 million tons of sulfur will become available from oil shales and coal gas, giving a total cumulative production of 400 million tons. The cumulative demand in the U.S. is estimated to be 550 million tons by 2000 A.D., leaving a deficit of 150 million tons of sulfur (513.95 million tons of H_2SO_4).

Based on data in Table 2, about 0.943 ton of sulfur is required as sulfuric acid per ton P_2O_5 produced as wet-process phosphoric acid. The U.S. is producing 6.248 million tons of P_2O_5 (1974) as wet-process acid. The TVA projection for 1980 U.S. production is 10.016 million tons of P_2O_5 .¹¹ Assuming that a median value of about 9.8 million Btu as natural gas (9800 ft³) are required for mining a short ton of sulfur then it can be estimated that about 7 million Btu are required per short ton of P_2O_5 to produce wet-process phosphoric acid from Frasch sulfur. Recovering sulfur from fuels would therefore not only conserve our natural sulfur reserves but would also reduce the energy requirement needed for mining.

The Impact of Abatement Sulfur on the Sulfur Market

The Frasch sulfur industry is dominated by a small number of large producers. The industry is concentrated and production is centralized in a few mines located within a small region of the Texas and Louisiana Gulf Coast. The marketing system is highly organized and specialized. It has the flexibility of marketing either elemental sulfur or sulfur in the form of sulfuric acid. It is recognized that

expanded rates of extraction of sulfur reserves will come about only with increasing supply costs. The sulfur producers are in an excellent position to balance the rate of development of the reserves in the Frasch mining industry with the production and marketing of abatement sulfur byproducts. In the long run, sulfur reserves could be used to smooth out short-run fluctuations in supply and demand.

Assuming the sulfur industry finds it profitable to absorb the abatement products into its marketing system, then little disorder or disequilibrium in the market would result. This is especially true since the existing industry already serves a majority of the sulfuric acid manufacturers in industrial chemicals as well as the fertilizer industry. In this market, sulfur is traditionally sold on a contract basis directly to industrial users where it is used predominantly in the form of sulfuric acid. Current reserves provide reliability of supply essential to the contract consumer.

If the sulfur producer does not choose to develop the market for abatement sulfur byproducts, then an alternate strategy might be the establishment of a formal commodity exchange. This would involve considerable reorganization but would assure utilization of abatement sulfur byproducts in a competitive market.

THE EXISTING SULFURIC ACID INDUSTRY

Sulfuric acid is produced by burning sulfur or sulfur-bearing materials to form SO_2 . Sources of sulfur or SO_2 for the manufacture of sulfuric acid include (1) elemental sulfur, (2) pyrites, (3) gypsum, (4) petroleum products, (5) smelter off-gases, and (6) waste gases from burning fossil fuels. In 1973 a brimstone-based acid accounted for 82.5% of the total sulfuric acid production, followed by pyrite-based acid at 3.1% and all other raw material sources at 14.4%. Thus far, this study focuses on acid plants burning elemental sulfur.

The estimated end uses of sulfuric acid for 1975 are presented in Table 3. These data indicate that the manufacture of phosphate fertilizers requires more than half of the sulfuric acid used in the U.S.

Table 3. SULFURIC ACID-CONSUMING INDUSTRIES IN THE U.S.
(000's of net tons, 100% H₂SO₄)

Consuming industries	1975	
	Ton	%
Fertilizer industries		
Phosphatic fertilizers	16,900	51
Ammonium sulfate or other	2,280	7
	<u>19,180</u>	<u>58</u>
Other industries		
Chemicals	3,830	12
Petroleum refining	1,880	6
Iron and steel	530	1
Other metals	1,300	4
Paints and pigments	1,160	3
Rayon and cellulose film	860	3
Miscellaneous	<u>4,260</u>	<u>13</u>
Total	33,000	100

U.S. production of sulfuric acid in 1973 was 31.7 million tons (100% H₂SO₄) which is about 80% of the total production capacity in the U.S. (47 million tons). About 59% of production capacity was committed to captive use. Only about 12.9 million tons were externally marketed from the 1973 production. Although there has been little growth in new sulfuric acid production in the period 1966-1973, there has been a shift in the geographical location of acid production. During this period, production of new acid in the north central states declined from 4.5 to 3.7 million tons, but production of new acid in Florida and Louisiana increased from 8.8 to 12.3 million tons. This shift in location is due to the recent increase in phosphate fertilizer production in the Gulf Coast area, especially in Florida and Louisiana.

The long-term growth in acid consumption in the U.S. has been about 4-6%/yr and has been closely tied to the fertilizer growth pattern. In recent years, however, the world market for sulfuric acid has increased rapidly -- and further growth in international trade has been predicted.¹² The trend started in 1965 and by 1973 world trade had increased fivefold -- to 2.5 million tons. Acid is fast becoming as important as pyrites (sulfide ores) in terms of the overall world trade in sulfur-containing materials. The trend is away from trade in pyrites toward trade in pyrites-based sulfuric acid. New economies realized, in transport of sulfuric acid by sea have been a key factor in the recent evolution of the world acid trade pattern.

Existing Contact Acid Plants in Eastern U.S.

TVA's computerized file of worldwide manufacturers of fertilizer and related products contains a list of 209 U.S. sulfuric acid plants producing acid by burning elemental sulfur. Total annual production capacity exceeds 47 million tons. Only those acid plants located east of the Rocky Mountains were considered as a potential market for abatement acid. This reduced the list to 166 plants with an annual production capacity of 42.9 million tons. The geographic distribution of these plants by states is outlined in Figure 2 and in Table 4.

Table 4. EASTERN U.S. SULFURIC ACID PLANT CAPACITY (1975)
(000's Short tons -- 330 Days per annum)

<u>State</u>	<u>Number of Plants</u>	<u>Annual Capacity</u>	<u>State</u>	<u>Number of Plants</u>	<u>Annual Capacity</u>
Alabama	5	455	Minnesota	1	107
Arkansas	4	584	Mississippi	3	1,250
Colorado	1	40	Missouri	3	581
Delaware	1	360	New Jersey	10	2,300
Florida	22	16,552	New York	1	6
Georgia	10	768	North Carolina	8	1,885
Illinois	15	2,176	Ohio	8	844
Indiana	3	713	Oklahoma	1	90
Iowa	3	651	Pennsylvania	4	437
Kansas	3	265	Rhode Island	1	20
Kentucky	2	218	South Carolina	6	134
Louisiana	11	6,206	Tennessee	5	578
Maine	1	75	Texas	13	3,876
Maryland	3	465	Virginia	9	733
Massachusetts	1	140	West Virginia	1	135
Michigan	4	168	Wisconsin	1	17
			Wyoming	2	100
		Total plants	166		
		Total annual capacity	42,929		

The Impact of Abatement Acid on the Sulfuric Acid Industry

Sulfuric acid plants are widely scattered throughout the U.S. chiefly because of the low bulk value of the acid, difficulties of handling the acid in the bulk, and subsequent high cost of shipment as compared to handling elemental sulfur. Therefore, acid has been



Figure 2. Geographic distribution of sulfuric acid plants and marketing terminals (1975).

traditionally produced by sulfur-burning plants near the point of consumption in captive use. However, many existing plants are old and will soon need replacing. Some will shut down in 1975 because compliance with pollution control regulations may not be economical. Producers in this situation will like the opportunity to buy abatement acid in lieu of building a new acid plant.

Many power plants enjoy a unique location advantage for supplying abatement acid in the existing market. This is especially true for acid plants located in areas remote from traditional sulfur supplies. Therefore, the most orderly way to incorporate the abatement acid would be to replace first the capacity of sulfur-burning sulfuric acid plants remotely located from sulfur sources. In this instance the relatively high-cost producer is given the opportunity to close his plant and buy abatement acid at a saving. The more efficient and better located plants continue to produce in status quo.

Production Costs for Sulfuric Acid

To put realism in such a marketing approach, some estimate is needed of the costs that could be saved or avoided by existing acid producers. Such costs are delineated below:

Raw material.....Sulfur

Utilities.....Electric power
Cooling water
Processed water
Boiler-feed water

Operating expenses...Labor
Supervision

Capital costs.....Amortized costs for maintenance of
existing facilities and amortized
costs of new capital investment at
end of useful plant life

In the Phase I study, a computer algorithm was developed using these inputs and others to calculate contact sulfuric acid production costs. Details of this program are given in the report on Phase I. The unique concept incorporated into this model relates to the method used for handling existing plants as compared to the traditional static analysis used to justify the investment in a new plant. For existing plants, the initial capital expenditures are handled as a "sunken in-

vestment" and, therefore, do not enter directly into the firm's decision to discontinue present production and buy abatement sulfuric acid. Only avoidable costs are considered in making this decision.

Annual costs are calculated in perpetuity using the discounted cash flow analysis method. The outlay streams are then amortized or averaged over all years in the firm's planning horizon. The cost streams are composed of (1) constant annual expenditures for sulfur, utilities, and operating expenses, (2) periodic expenditures for new plants, and (3) maintenance of existing facilities which is assumed to grow at a compound rate. The impact of inflation is not included in the analysis. These cost streams for a new plant are presented in Figure 3.

The optimum useful life is identified as the minimum point on the average total cost curve. At this point the added capital cost savings enjoyed by increasing useful life by 1 yr equals the added maintenance saving from shortening useful life by 1 yr. The average capital charge of 19.3%, identified in Figure 3, covers a range of from 23 to 36 yr. Possibly random effects, such as abrupt physical, economic, technological, or environmental changes, play the dominant role during this period with regard to the timing of plant replacement or shutdown.

Sulfuric acid plants built prior to 1960 were assumed to average 95.5% conversion of sulfur to acid. Plants built between 1960 and 1975 are assumed more efficient with 97% conversion. These efficiencies, however, are not representative of plants that must operate after 1975 since emission limitations will require an efficiency of at least 99.7%. As for the potential growth market, it will be necessary to consider tail gas cleanup at a 99.7% efficiency level for new plants (double absorption). Capital and operating cost estimates for acid plant tail gas cleaning systems for existing plants have been completed but are not yet incorporated accurately in the model. These costs, of course, must be added to the avoidable costs of existing plants.

The major variables used in the acid plant cost generation program are outlined in Table 5 which contains sample parameters associated with each variable. The results of this program are plotted as a demand curve for abatement acid in Figure 4. The avoidable costs (theoretical) are calculated at each respective acid plant location considered.

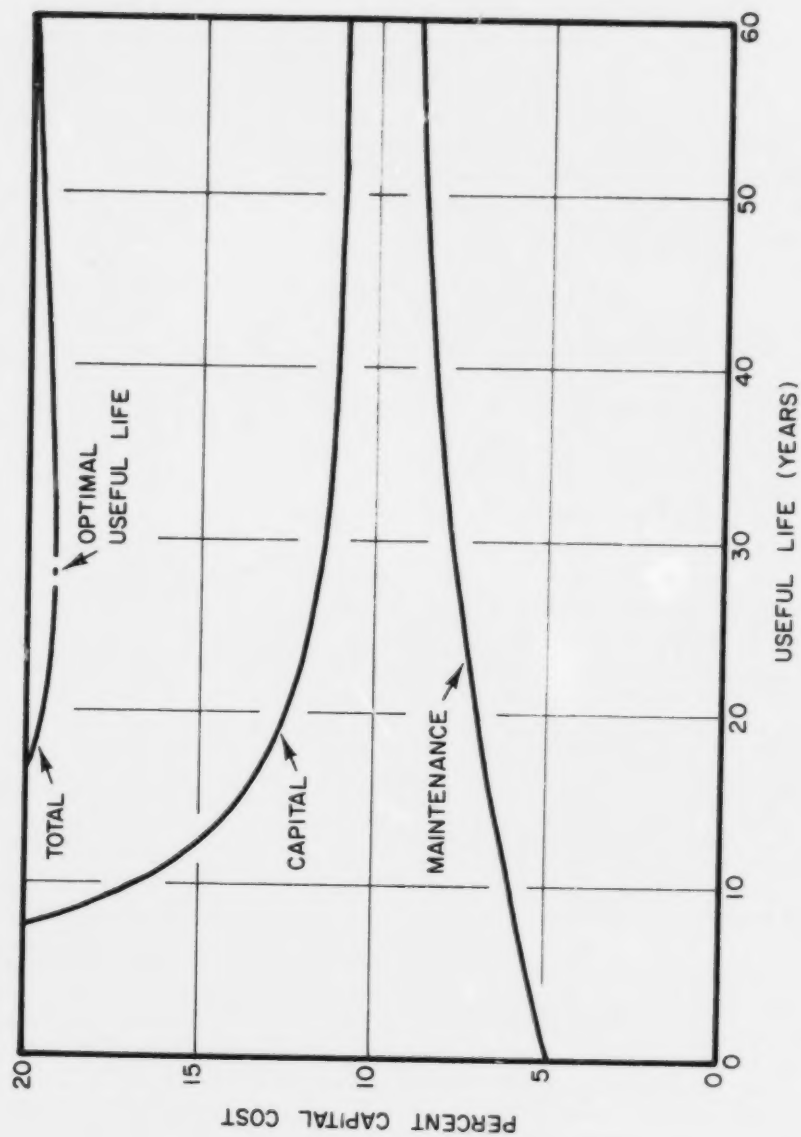


Figure 3. Amortized value of maintenance and capital outlays for new plants (assuming 11% interest and 5% compound maintenance).

Table 5. MAJOR PARAMETERS IN MODEL

No.	Description of variable	Example value	
1	Tons of sulfur per ton H_2SO_4 (before YEAR60)	.3053	PRE60
2	Tons of sulfur per ton H_2SO_4 (after YEAR60)	.3006	POST60
3	Year of technology change	60.	YEAR60
4	Sulfuric acid plant investment (\$/ton-yr)	27.285	EXPENDO
5	Capacity for this plant (000's tons/yr)	247.5	SIZEO
6	Scale factor for determining investment for other sized plants	.734054	FACTOR
7	Fixed conversion cost per ton (\$/ton)	.47	AVC
8	Fixed annual conversion cost (\$/yr)	116.620	FC
9	Taxes and insurance rate	.015	TIR
10	Time preference rate for money	.11	RATEI
11	Compound maintenance rate	.05	RATEM
12	Economic useful life	34.	USELIFE
13	Percent H_2SO_4 concentration	98.	ACDCON
14	Port Sulphur price (\$/short ton)	53.57	PS
15	Steam plant H_2SO_4 price (\$/ton H_2SO_4)	0.	PA
16	Proportion of 330 TPD capacity estimate	1.	DEMAND
17	Number of steam plants	610.	N
18	Number of acid plants	166.	M
19	Number of years considered	1.	NYEARS
20	Years considered	75.	YEAR(I)

The Demand Curve for Abatement Acid

The March 1975 price for sulfuric acid (100% H_2SO_4 f.o.b.) was \$44.95/ton.⁸ This represents a 37% increase since April 1974 (\$32.75). Cost estimates used for each specific acid plant are depicted in Figure 4. Costs of manufacture range from \$28 to \$45 depending upon plant location, size, and age.

For illustrative purposes it is useful to consider the demand curve for abatement acid that would be traced out by a uniform f.o.b. acid plant supply cost if acid supply location in Figure 2 were ignored. This demand curve is estimated by ranking all acid plants from highest to lowest cost and accumulating demand quantities as shown in Figure 4. At a very high supply cost from power plant producers, only a few plants would be better off buying rather than producing sulfuric acid. These plants tend to be old, low-volume producers far from sulfur supplies.

SULFURIC ACID DEMAND CURVE

1 DEMAND

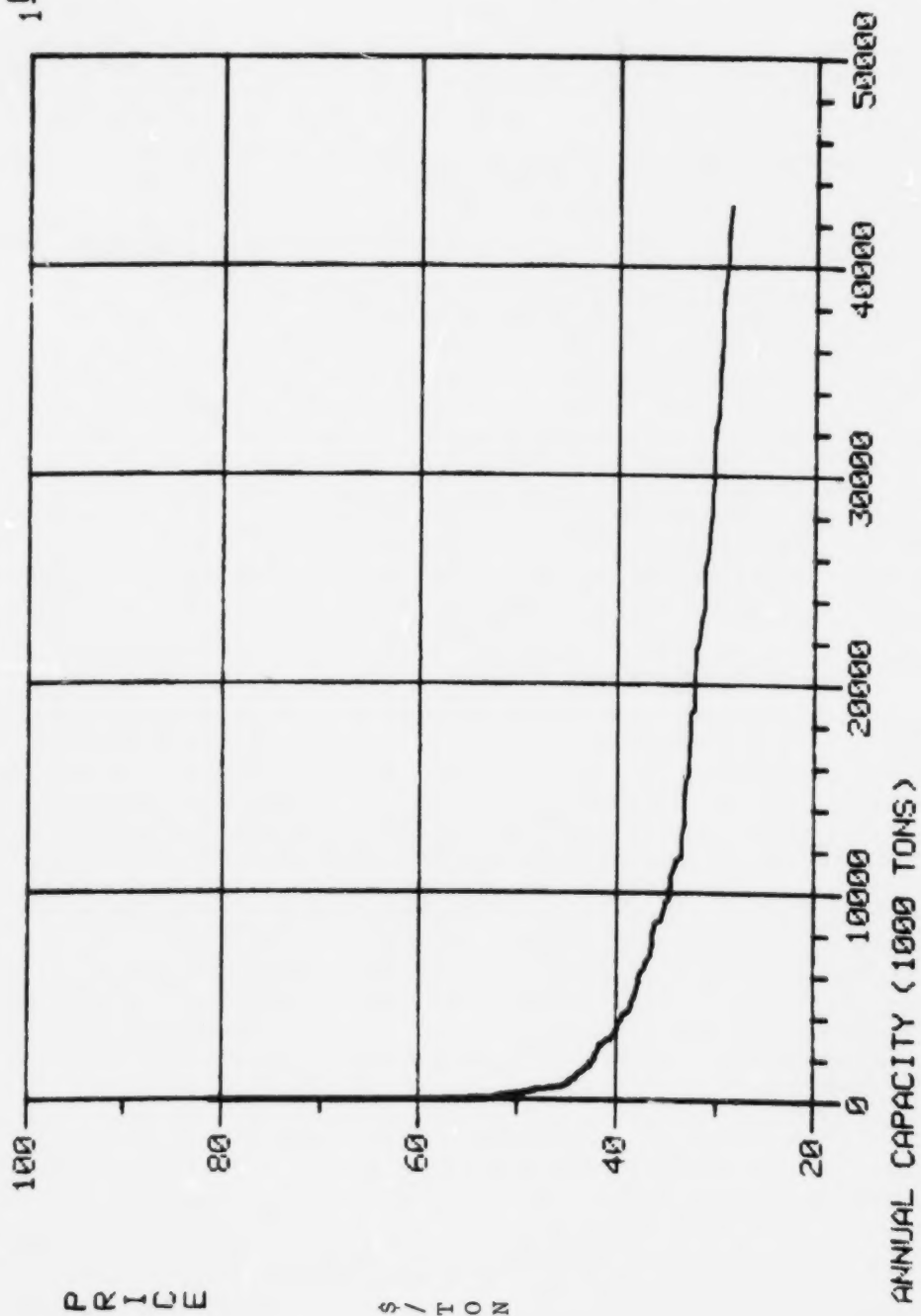


Figure 4. Abatement byproduct sulfuric acid demand curve.

As supply cost declines, very high-cost producers disappear rapidly and the demand curve for abatement acid flattens. At low supply costs from power plants, all but the largest, most modern acid plants located near sulfur supplies would buy rather than continue production. Small quantities of abatement acid could then be marketed at high value but as the supply increases the value declines.

POTENTIAL ABATEMENT PRODUCTION OF SULFUR AND SULFURIC ACID FROM POWER PLANTS

In assessing potential abatement byproduct production, only emissions from power plants have been evaluated. Figure 5 shows the locations of major coal- and oil-fired power plants. Important design and operating characteristics of these plants are available from FPC through published reports.^{13,14} These data are compiled each year from FPC Form 67 which the utilities file with FPC. With these data it is possible to project the amount of sulfur byproducts that could have been produced each year in the U.S. The latest data available from FPC are for 1972; however, they can be updated annually. FPC has asked for 5- (1978) and 10-yr (1983) projections with the 1973 data items. TVA has contracted with FPC to obtain these projections for use in this study.

Federal-State Air Quality Standards

Not all 2,564 power plant boilers in the U.S. require more air pollution control measures. Under the Clean Air Act Amendments of 1970, EPA has set both primary and secondary ambient air quality standards to be met by mid-1975. There are also Federal emission standards for new sources in operation after 1975. To meet these standards, the Federal government has asked each state to propose its own implementation plans for the 247 Air Quality Control Regions (AQCR). Each SIP would be reviewed by EPA, then approved or returned to the state with suggested revisions.

A list of the states and their strategies is given in Table 6. Some states have more than one strategy listed; this occurs when special situations such as a concentration of power plants and industries in one AQCR make more than one strategy desirable.

A review of the status of SIP showed that the states have proposed several methods for meeting the Federal ambient air quality standards. These have been classified into 10 groups outlined in Table 7.

Only a few emission standards for SO₂ from fossil-fueled steam-electric generating plants have been agreed upon by both the Federal and state governments. Other SIP are being argued in the courts or are being negotiated by the states and the Federal government. Some states have not issued SIP.

Table 6. INDEX OF STRATEGIES FOR CONTROL OF SO₂ EMISSIONS BY STATES

State	Strategy ^a group number	State	Strategy ^a group number
Alabama	3	Nebraska	3
Arizona	4	Nevada	1, 2, 3, or 5
Arkansas	8	New Hampshire	2 or 6
California	2 or 7	New Jersey	2 or 4
Colorado	9	New Mexico	3
Connecticut	1 or 3	New York	2 or 4
District of Columbia	2	North Carolina	3
Delaware	2 or 8	North Dakota	3
Florida	4	*Ohio	10
Georgia	2	Oklahoma	8 or 4
Hawaii	1	Oregon	7 or 2
Idaho	2	Pennsylvania	2 or 3
Illinois	4	Puerto Rico	1
*Indiana	10	Rhode Island	5 or 3
Iowa	4	South Carolina	3
Kansas	9 or 5	South Dakota	3
Kentucky	4	Tennessee	3 or 4
Louisiana	7	Texas	8
Maine	1	Utah	2
Maryland	2	Vermont	1
Massachusetts	6	Virginia	3 or 7
Michigan	2	Washington	3 or 7
Minnesota	2	West Virginia	3
Mississippi	3	Wisconsin	8 or 4
Missouri	1 or 3	Wyoming	8
Montana	2		

^a See Table 7 for description of strategies

*Note SIP not enforceable (because of court action or other reason in March 1975).

Table 7. STRATEGIES FOR STATE IMPLEMENTATION PLANS

Group No.	Type of state strategy proposed
1	% S for all fuels combined
2	% S for an individual fuel type
3	lb SO ₂ /million Btu for all fuels combined
4	lb SO ₂ /million Btu for an individual fuel type
5	lb S/million Btu for all fuels combined
6	lb S/million Btu for an individual fuel type
7	ppm SO ₂ emission regulation
8	ppm SO ₂ ambient air quality standard
9	no SIP
10	SIP not enforceable (because of court action or other reason)

SIP regulations can be determined accurately; however, this constraint is dynamic over time. Regulations can change or be in litigation. (Indiana and Ohio were in litigation in March 1975 and were excluded from this study.)

By applying SIP, a reasonable assessment of the upper limit for abatement byproduct production from power plants can be made; however, another more stringent screen is needed to define rational quantities.

Selecting Most Promising Candidate Boilers for Abatement Production

With the large data base available from FPC Form 67, it should be possible to create a more accurate screen to center on the most promising candidates for abatement byproduct production. Earlier work by TVA for EPA in preparing detailed cost estimates for the five leading FGD processes⁴ offers the best potential as a basis for development of a final screen. Completed in 1975, the referenced report contains well-defined investment and operating cost estimates of the five leading FGD systems based on key power plant design and operating parameters. The five processes are listed as follows:

Limestone slurry scrubbing

Lime slurry scrubbing

Magnesia slurry scrubbing -
regeneration of H_2SO_4

Sodium solution scrubbing -
 SO_2 regeneration and reduction to sulfur

Catalytic oxidation

In the EPA-TVA cost report, two of the processes (the magnesia slurry scrubbing - regeneration process producing 98% sulfuric acid and the sodium solution - SO_2 reduction process producing elemental sulfur) produce saleable byproducts covered in this study. The costs of these processes can be compared with those of the throwaway limestone slurry scrubbing process in deciding what scrubbing strategy is to be adopted for each boiler or plant where appropriate. The detailed investment and operating cost projections given and the method illustrated for scaling costs are suitable for projection of costs of the processes at other capacities based on comparable FPC operating characteristic data.

The three scrubbing processes selected above for analysis in this paper will be referred to as (1) limestone slurry scrubbing, (2) magnesia (MgO) slurry scrubbing, and (3) sodium solution scrubbing.

To serve as an economic screen, power unit operating characteristic data from the FPC file and cost data for the limestone, magnesia, and sodium scrubbing processes were combined in a computer subprogram to project the investment requirements and operating costs on a boiler-by-boiler basis. The following data within the FPC file were used in this procedure:

1. Power unit size, MW
2. Boiler startup, yr
3. Power unit heat rate, Btu/kWh
4. Design coal feed rate, tons/hr
5. Heat value of coal, Btu/lb
6. Sulfur content of coal, lbs S/lb coal
7. Annual coal consumption, 10^3 tons/yr
8. Design oil feed rate, bbls/hr
9. Heat value of oil, Btu/gal
10. Sulfur content of oil, lbs S/lb oil
11. Annual oil consumption, 10^3 bbls/yr
12. Total air rate to boiler, scfm
13. SO₂ recovery unit startup, yr
14. Power unit status, new or old

The program uses an operating capacity factor calculated from FPC data for the 1972 calendar year.¹⁴ Depreciation and capital charges included in the annual operating cost projections are based on a total depreciable power plant life of 30 yr as recommended by FPC. The SO₂ removal facilities for existing plants are, therefore, depreciated over a period equal to the remaining life of the power unit. For plants more

than 30 yr old, whose remaining life could be calculated to be negative, depreciation and capital charges are based on a 1-yr depreciation period. Waste disposal pond size and costs for the limestone slurry process are scaled proportional to the remaining life of the power unit.

In projecting the investment and annual operating cost of scrubbing systems on each power unit for each run of the program, the results show the boilers for which SO_2 removal is the most economical in order of increasing unit operating costs (either \$/ton 100% H_2SO_4 or \$/ton elemental sulfur), and the relative difference in unit operating costs for pollution abatement by the three processes, i.e., (1) H_2SO_4 production, (2) elemental sulfur production, or (3) limestone throwaway. Also, by incorporating the unit operating cost for each boiler in the production-distribution model, a more realistic market potential for each abatement product can be defined. One weakness of this screen yet to be overcome is the need for a retrofit difficulty factor covering each site specific application. Some power units are more difficult to fit with scrubbers than others. The screen still enables a decision of the best scrubbing option to be made on a boiler-by-boiler basis. But each boiler's relative competitive position with others cannot yet be made accurately.

Potential Abatement Production on Boiler Basis

Based on SIP regulations outlined above, total emissions can be calculated for all plant boilers in the model exceeding the allowable emissions. This amounts to 154 plants (610 boilers) emitting a total of 10.83 million tons of equivalent 100% H_2SO_4 . If one calculates the tons of H_2SO_4 emissions allowed by existing (March 1975) SIP standards (5.80 million tons H_2SO_4) and subtracts this quantity from total emissions, then the actual amount to be controlled is identified. This amounts to 5.03 million tons (10.83 - 5.80) of H_2SO_4 . However, once the decision is made to scrub a boiler the technical requirements to operate a flue gas scrubbing system are imposed. The model assumes that the FGD system would remove 90% of the SO_2 emissions. Therefore, from the total emission of 10.83 million tons of H_2SO_4 , 9.75 million tons of H_2SO_4 could be produced with installations of FGD systems on all boilers exceeding SIP standards. This amounts to an over control of 4.72 million tons (9.75 - 5.03) of abatement H_2SO_4 production.

Program Analysis at the Boiler Level

Results of the program run that identified the unit cost of operating three different FGD systems on each of the 610 boilers are outlined in Figures 6 and 7. In Figure 6, the unit costs vary from \$0 to >\$999,999.00. The reason for the extreme range is that the amount

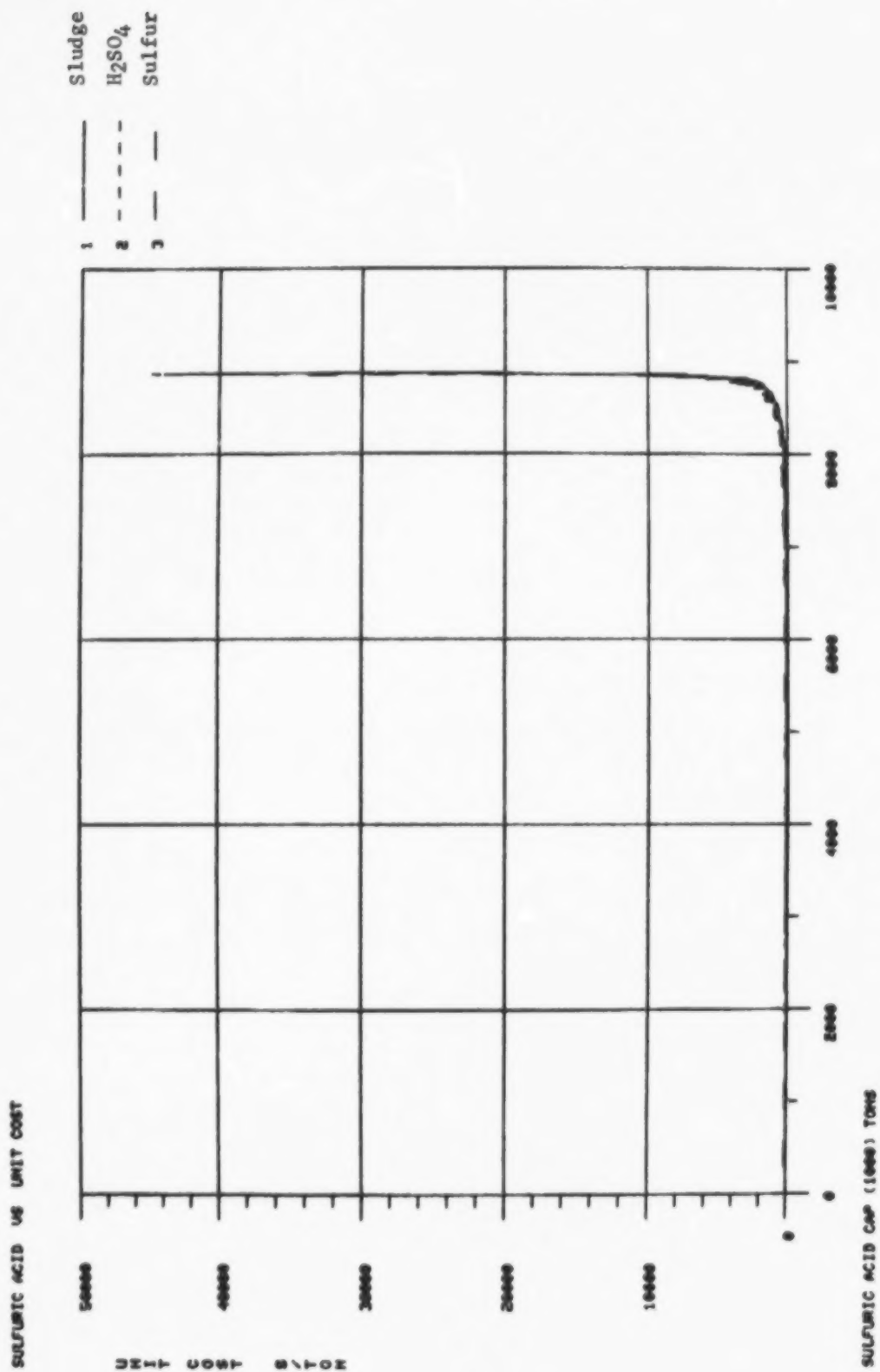


Figure 6. Unit production cost for abatement products for eastern U.S.

SULFURIC ACID US UNIT COST

- 1 Lime (Sludge)
- 2 MgO (H_2SO_4)
- 3 Sodium (Sulfur)

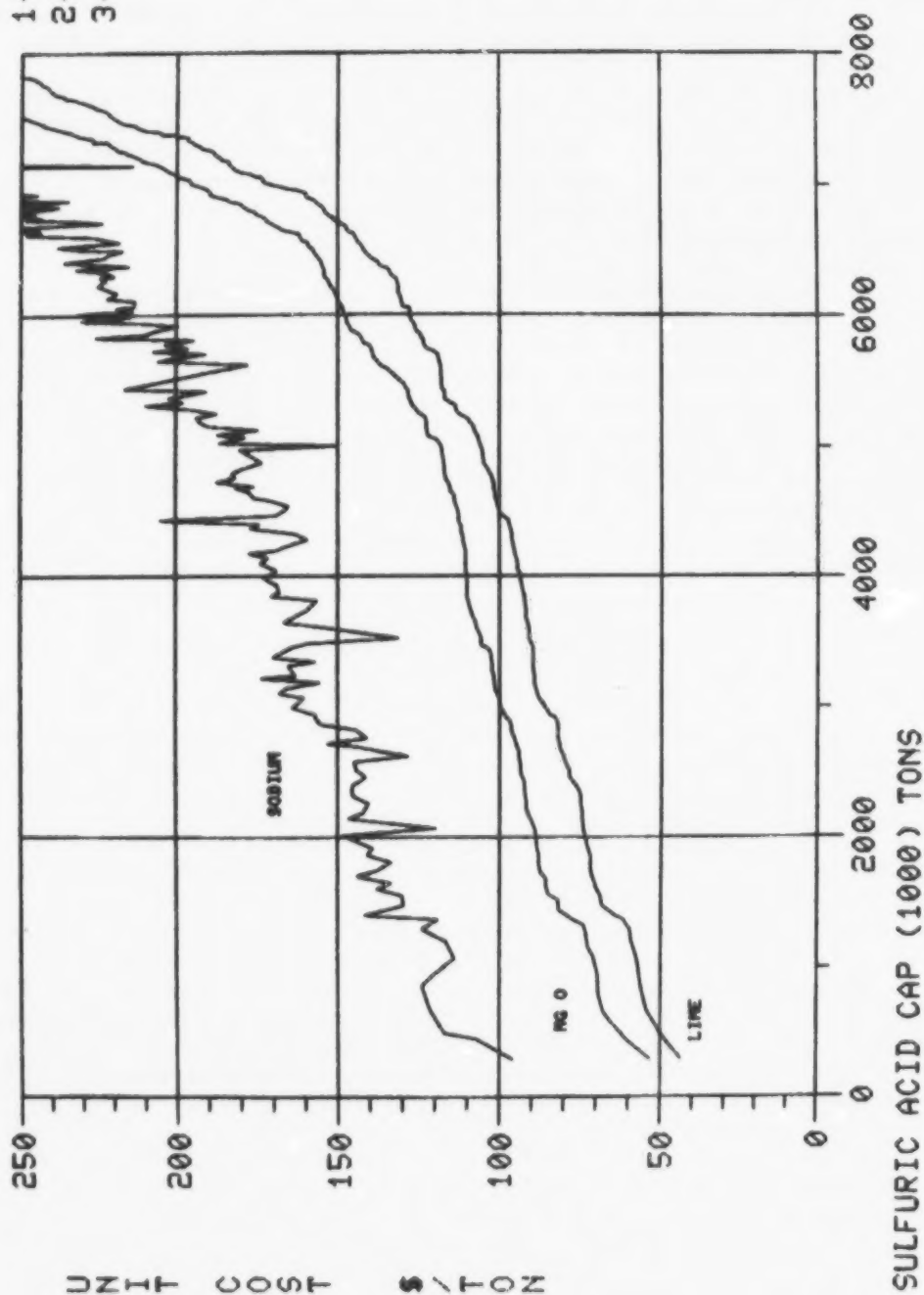


Figure 7. Unit production costs for abatement products.

of abatement acid which must be scrubbed from the boilers to meet SIP standards ranges from 318,963 tons/yr for the lowest unit cost boiler down to 1 ton of abatement acid for the highest unit cost boiler. The model assumes that if a boiler exceeds SIP standards in any quantity, then the cost of operating a scrubber is imposed. Instead of scrubbing, the high cost boilers would probably turn to clean fuel substitution.

The comparative cost of the three scrubbing systems is depicted on a smaller scale in Figure 7. The lowest unit cost boiler is identified at \$43.77/ton of H_2SO_4 equivalent (\$0.25/million Btu) for limestone slurry, \$53.05/ton of acid for magnesia, and \$98.73/ton of acid equivalent for sodium. (Multiply \$/ton of H_2SO_4 equivalent by 1.531 to get \$/ton of SO_2 removed.)

The sodium solution process is at a disadvantage in the model because of the relatively higher unit cost as compared with either limestone slurry or magnesia slurry processes. Figure 7 shows that on the average the sodium solution process for abatement sulfur is about \$50 - \$60/ton higher cost on an equivalent basis of 100% H_2SO_4 as compared to the magnesia slurry process for abatement H_2SO_4 . This prevents abatement sulfur from competing with abatement H_2SO_4 even at the optimum location considered in the model not counting the additional cost of converting the sulfur to H_2SO_4 . This raises the question of a conservation of energy principle. Is it a rational decision to reduce SO_2 to sulfur, then market the sulfur in processes that require oxidizing it back to SO_4 ? This study indicates a tentative negative answer.

Supply Curve for Abatement Acid

A demand curve for abatement acid was presented in Figure 4. For illustrative purposes it is useful to consider the supply curve that would be traced out by different levels of a uniform f.o.b. steam plant supply cost for sulfuric acid. Again, this ignores steam plant location relative to acid plants. Such a curve can be estimated by ranking power plant boilers from lowest to highest cost for producing sulfuric acid and accumulating supply quantities shown in Figure 7. Low-cost boilers would tend to be new, large plants which burn high-sulfur coal, while high-cost boilers would tend to be old, small, and inefficient. The only boilers shown in Figure 7 are those exceeding SIP standards since others would probably not enter the supply picture. Note that the range of supply costs is much greater than those for demand. While about 9 million tons of acid are available at an infinite price, supplies greater than about 8 million tons are unreasonable.

While a few large modern boilers are reasonable candidates for scrubbing, supply costs increase rapidly as more and more boilers

pursue this alternative. It is unreasonable for all boilers to use a scrubbing strategy.

Summary of Operating Characteristics of Power Plants in Eastern U.S.

Data from FPC Form 67 were loaded on MRI System 2000 to provide an improved data management system for the operating characteristics of each power plant boiler. The scrubbing cost data calculated for each boiler in the unit cost subprogram discussed above were also added to System 2000 as well as an indication that a given boiler did or did not meet the SIP.

Table 8 shows selected operating characteristics for all fossil-fuel-fired boilers located in eastern U.S. in 1972. Column 2 contains all boilers having emissions exceeding SIP standards. Column 3 and 4 contain the boilers selected by the two scrubbing cost screens used in model runs. Total abatement capacity for all plants is 22.292 million tons as compared with 9.748 million tons for the plant exceeding SIP.

Boilers with emissions exceeding SIP standards tend to have greater generating capacity, fuel consumption, average H_2SO_4 abatement capacity, and plant boiler factors. The average sulfur content of fuels is also greater. The age distribution, however, is uniform for both groups on a percentage basis. The last two columns relating to boiler scrubbing cost screen for model runs will be discussed in the model analysis.

ABATEMENT PRODUCTION-DISTRIBUTION-TRANSPORTATION SYSTEM

To assess representative competitive costs, this market system analysis must generate accurate sulfur freight rates from the Frasch sulfur sources to the acid plants and sulfuric acid freight rates from all power plants to all sulfuric acid plants. This represents more than 300,000 possible rates. Also, the overall market study series calls for a possible expansion to evaluate calcium sulfate for wallboard, ammonium sulfate, and several other fertilizer classifications.

Standard Point Location Code

The logistical linkage between the sulfuric acid and power plant data bases and the rate generation system is the Standard Point Location Code (SPLC). This is a transportation-oriented, six-digit number prescribed by the National Motor Freight Traffic Association under the guidance of the SPLC Policy Committee. The system is similar

Table 8. OPERATING CHARACTERISTICS OF POWER PLANTS IN
EASTERN U.S. (SPLC <700000) (1972)

	All boilers	Boiler emissions >SIP	Boiler scrubbing cost screen for model runs	
			Unit cost MgO <\$100	Unit cost limestone <\$175
No. of: Utilities	182	57	18	37
Plants	597	154	25	73
Boilers	2,564	610	38	169
H ₂ SO ₄ abatement capacity, tons	22,292,127	9,748,274	3,285,710	7,749,216
Average H ₂ SO ₄ abatement capacity, tons	10,373	15,981	86,466	45,853
Average coal consumed, 1000 tons	980	1,115	1,835	1,567
Average oil consumed, 1000 bbls	897	1,176	21	529
Coal-sulfur content average, %	2.4	3.0	3.6	3.1
Oil-sulfur content average, %	0.7	0.8	0.3	0.4
Associated generating capacity average, MW	135	158	403	263
Plant boiler factors average, %	51.7	55.1	64.1	63.8
Age of boilers, %				
0-5 yr	10	9	42	23
6-10 yr	7	8	34	21
11-15 yr	12	13	21	27
16-30 yr	39	43	3	29
Over 30 yr	32	27	0	0

to U.S. mail zip codes. Figure 8 shows location areas to the first two-digit level. The first digit indicates a region relating to major traditional traffic associations. The first two digits uniquely identify a state or a portion thereof. As more digits are added, smaller nested areal units are identified. The third digit gives a cluster of counties, the fourth digit a county, the fifth digit a cluster of points within a county, and the sixth digit identifies all rail and truck specific points.

Distribution Cost Generation

A logic flow diagram of the freight rate generation system used in this model is shown in Figure 9. It shows that an SPLC for a power plant origin and one for a sulfuric acid plant destination are input to the National Rate Basis Tariff 1-C (NRBT 1-C). This tariff determines for rail rate purposes the basing points for the origin and destination. While there are about 60,000 rail points, there are only 2,632 basing points east of the Rocky Mountains (SPLC <700000).

Outputs from the NRBT 1-C block in Figure 9 are two sets of codes used to define mileage and tariff rates between the byproduct shipping origin and destination points. One set - Index 1 and Index 2 - is used to determine the appropriate rate base mileage to be applied. The two index values are pointers to a 3.5 million record triangular mileage file compiled from 12 tariffs resulting from the landmark 1945 Interstate Commerce Commission hearing entitled Docket 28300.¹⁵ The file includes rail (and some truck) tariff mileage for shipments within and between five major freight associations shown in Figure 10. Output from the Docket 28300 block of Figure 9 is a rate base number.

The second group of codes output from the NRBT 1-C define the mutually exclusive set (MES) numbers for the origin and destination points and serve as input to the Tariff Rate Generator block to choose the appropriate tariff. In Figure 10, locations of the nine major MES numbers east of the Rockies are shown. These result from considerable overlapping occurring among the five major freight associations. There are 19 mutually exclusive sets of basing points in the Docket 28300 tariffs. Table 9 lists the basing points which define the remaining 10 MES numbers. Table 10 lists all MES numbers as rows and the 12 Docket 28300 tariff numbers as columns and indicates that each MES in each tariff either (1) did not occur (blank), (2) occurred as a headline point (H), (3) as a sideline point (S), or (4) as both a headline and sideline point (B). Depending on the tariff association originating the tariff, the headline point can be either the origin or destination of shipment. Given the MES for both the origin and destination it can be determined in which tariff(s) these points can be found, which is output from the Tariff Generator block in Figure 9.

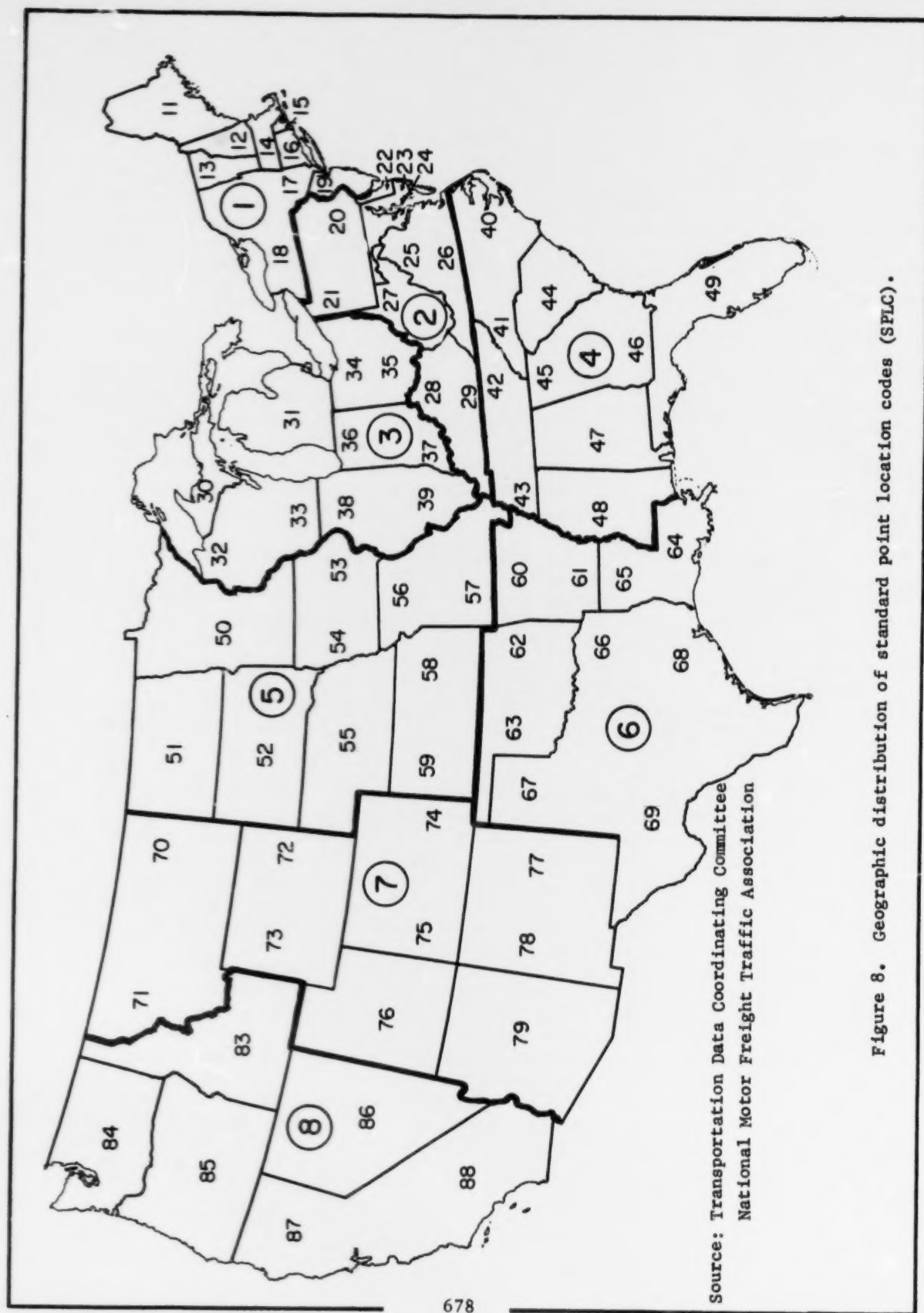


Figure 8. Geographic distribution of standard point location codes (SPLC).

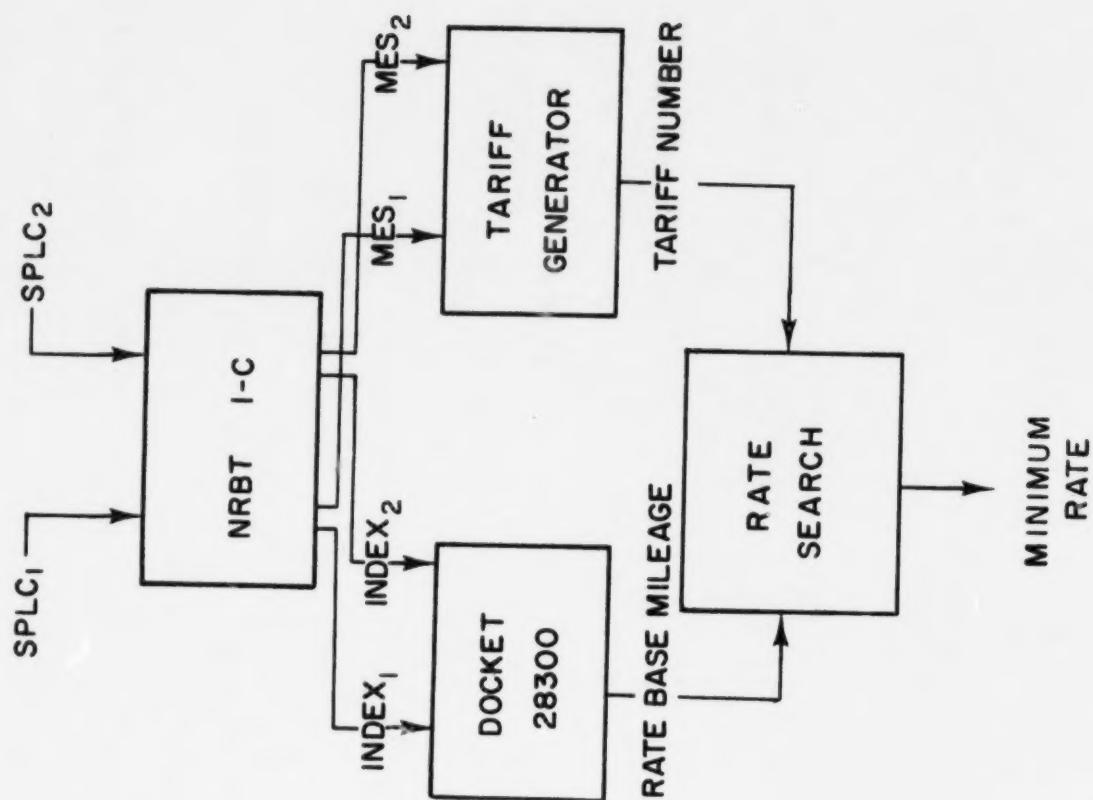


Figure 9. Flow diagram of freight rate generation model.

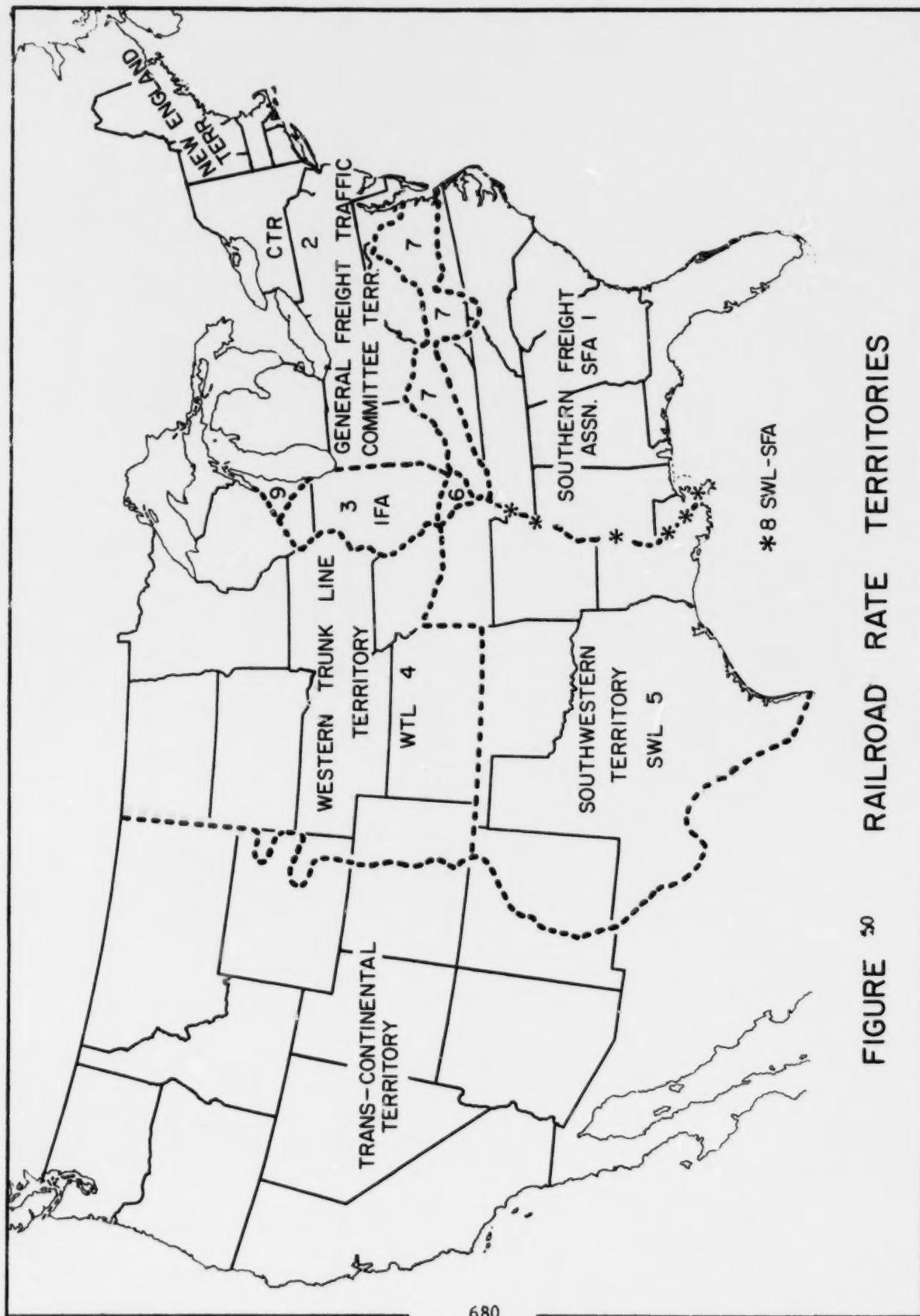


FIGURE 50 RAILROAD RATE TERRITORIES

Table 9. RECLASSIFICATION OF BASE POINTS

10	KY	LEXINGTON	14	VA	ST PAUL
10	KY	WINCHESTER	14	TN	BRISTOL
11	KY	CHILESBURG	15	SC	ANDERSON QUARRY
12	DC	WASHINGTON	15	SC	RION
12	VA	NORFOLK	16	NC	BUNN
12	WV	CHARLESTON	16	TN	BROWNSVILLE
13	VA	ALBERTA (S)	17	IL	SPARTA
13	VA	ALTAVISTA (S)	18	NY	PULASKI
13	VA	BURKVILLE (S)	19	IN	CANNELTON
13	VA	LYNCHEURG (S)	19	IN	CORYDON
13	VA	PETERSBURG (S)	19	IN	FERDINAND
13	VA	SUFFOLK (S)	19	IN	HUNTINGBURG
14	VA	BRISTOL	19	IN	MARENGO
14	VA	NORTON	19	WV	OLCOTT

Table 10. TARIFF GENERATOR

GIVEN TWO RATE BASIS POINTS FROM MUTUALLY EXCLUSIVE BASING POINT SETS MES AND MES₂, THEY CAN BE FOUND IN ONE OR MORE OF THE TARIFFS REPRESENTED BY COLUMNS BELOW, IF ONE APPEARS AS A HEADLINE (H) AND ONE AS A SIDELINE (S), WHERE BOTH (B) QUALIFIES AS HEADLINE AND SIDELINE

MES	TARIFF											
	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011
1		S		S		S		S	S	B	H	B
2									H	B		
3	B		B	H			S			B	S	
4	B	H					S					
5					3	H	H	H				
6	B		B				S			B	H	B
7						S			S	B		B
8		S		S	B							
9	B	H					S			B		B
10		S		S				S	S	B	H	B
11								S		B		B
12						S			H	B	H	B
13				S		S			S			B
14		S				S		S		B	H	B
15												B
16		S						S	S			B
17	B		B				S			B		B
18						S			H	B		B
19						S				B	H	

Figure 11 shows sulfuric acid rail rates within four major freight associations as a function of rate base numbers. A slight error in mileage is not nearly as critical as knowing which tariff applies. Also these are the only published sulfuric acid rates. Rates for the other eight tariffs were generated by TVA's Navigation and Regional Economics Branch from these using sound traffic legal arguments similar to the negotiation process that would insure should large acid movements become a reality. In Figure 9 rate base and tariff numbers are input to the Rate Search block and the minimum rate is output for use in the transportation cost model.

MARKET SIMULATION MODEL THEORY, ANALYSIS, AND RESULTS

Objective of the overall marketing model is to simulate long-run competitive equilibrium sulfur and sulfuric acid market conditions in the U.S. as might be impacted by clean air restrictions and available power plant scrubbing technologies which result in abatement acid or sulfur. To simulate these conditions, total cost of both the sulfuric acid and power industries is minimized subject to the condition that acid production (demand) is still met, either from traditional sulfur sources or with a partial substitution of abatement sulfuric acid.

The model is similar to the classic transportation model of linear programming where demands represent sulfuric acid plant customers and supplies represent either production at each of the commercial acid plants or purchases from any power plant boiler capable of producing acid. Incurred (transfer) costs represent either sulfuric acid production cost using Port Sulphur sulfur in the first case or boiler scrubbing cost plus transportation cost to the respective acid plants in the second case.

Economic Theory

Through the use of several simplifying assumptions, the complex process taking place in the model can be conceptualized in terms of classical supply and demand curves.

It was explained earlier, and summarized in Figure 4, that from the sulfuric acid plant data base and the long-run average acid production cost generator, all commercial acid producers can be ranked in terms of a demand curve. Assuming an average transportation cost, one might also conceive the price (cost) level being shifted down a certain number of dollars per ton to give a conceptual f.o.b. power plant acid demand curve such as DD' in Figure 12. At high abatement supply price levels, only the smallest, oldest, most remotely located acid plants would be interested in curtailing production and buying

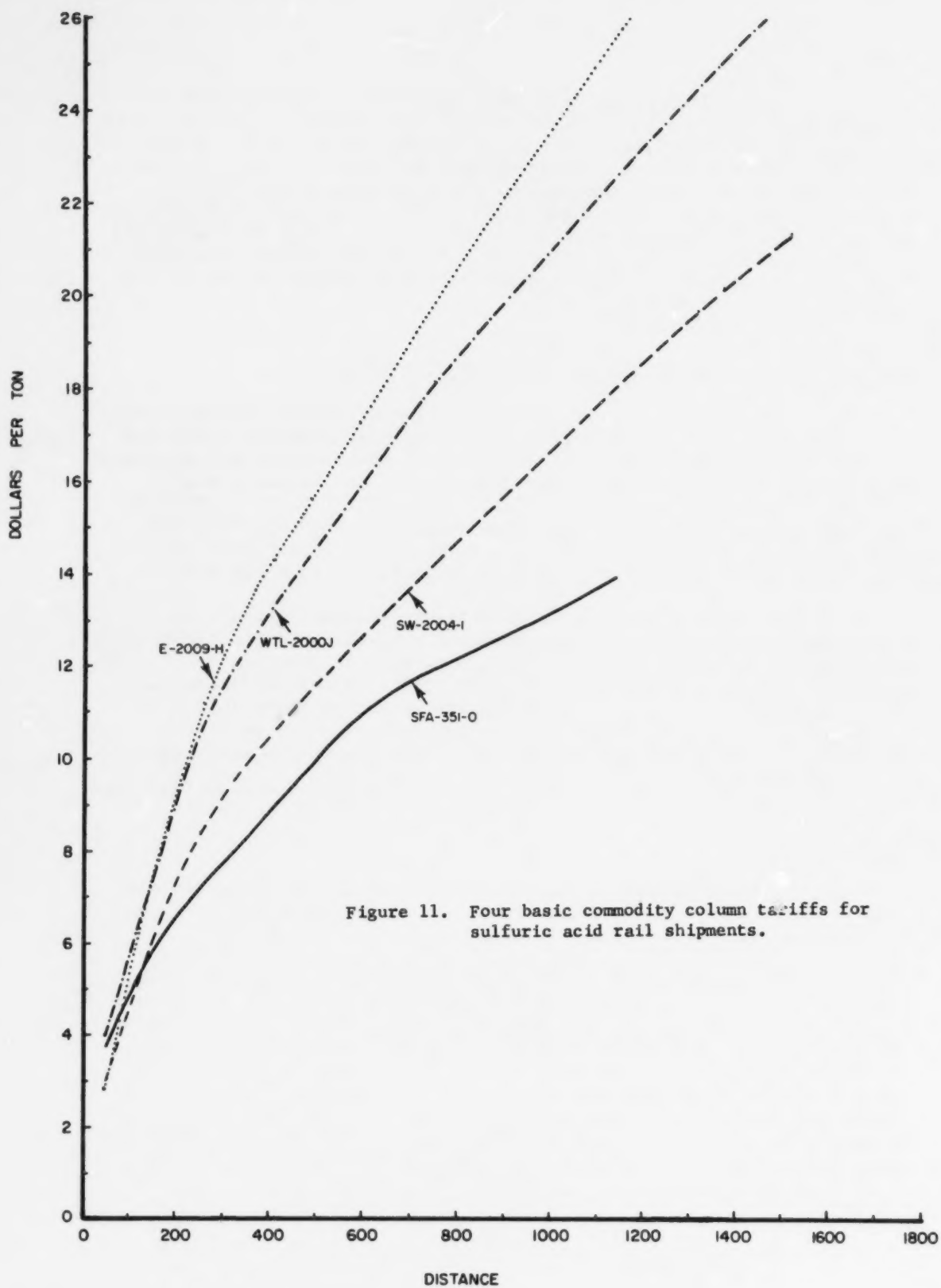


Figure 11. Four basic commodity column tariffs for sulfuric acid rail shipments.

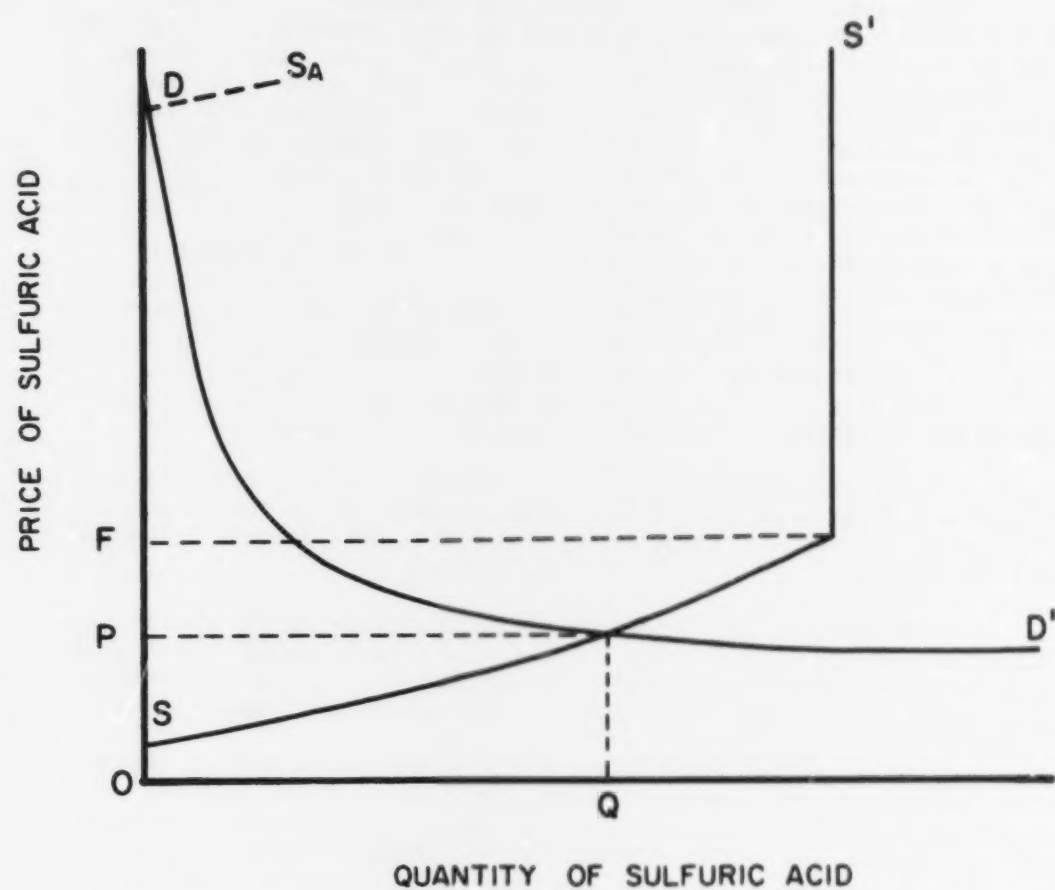


FIGURE 12: CONCEPTUAL DEMAND CURVE FOR SULFURIC ACID AND SUPPLY CURVE FOR ABATEMENT PRODUCTION.

abatement acid. As supply price declines, more acid producers buy until even the largest, newest plants located near sulfur supply sources become interested.

Likewise, as explained earlier and summarized in Figure 7, from the power plant data base and scrubbing cost generator, boilers can be ranked in terms of a supply curve, f.o.b. each power plant, such as SS' in Figure 12. The intersection of such a supply curve with the conceptual demand in Figure 12 would represent an equilibrium position. However, this intersection occurs at a very small tonnage (15,000 tons) because the abatement supply price level is so high. This is shown by a dotted line labeled SS_A in Figure 12. Applying a unit revenue adjustment parameter drops the level of the abatement supply curve, thereby producing a series of equilibrium intersections as increasing quantities of abatement production are considered. The supply curve SS' can be thought of as having a market adjustment (credit for pollution control cost) applied. Again the important concept to retain is that the supply curve slopes upward. At low demand prices only the largest, newest boilers would scrub even with the assumed market adjustment. As demand price increases, more marginal boilers become interested.

If spatial considerations could be ignored, the demand curve in Figure 4 and the supply curve in Figure 7 could be plotted on the same graph as in Figure 12; where they intersect would represent supply-demand equilibrium.

Looking first at the demand curve DD', those sulfuric acid producers above equilibrium price P would find it profitable to buy acid from steam plants rather than continuing production. Those less than price P would find it more profitable to continue production.

Looking at the supply curve SS', boilers below price P would find it feasible to use a scrubbing strategy that produces sulfuric acid, while those above price P but less than price F would profit from using a scrubbing strategy that produces and disposes calcium sludge. Those above price F would find it more profitable to use a clean fuels strategy in lieu of scrubbing.

Multidimensional Equilibrium Model

While the preceding simplified economic theory presents the essence of the economic model, a more elaborate spatial equilibrium model is required for realistic analysis. The problem is that the lowest acid cost boiler could be close to or far from the highest cost commercial acid plant. It, therefore, only makes sense to trace a demand curve for a single source of supply. This could be done for every supply point, but would be of no analytical significance unless there

was only one supply point being considered. As soon as more than one supply point is considered, they become competitors for lucrative demand points. Hence, while traditional supply-demand concepts are helpful in exploring the basic underlying economic structure of flue gas marketing alternatives, a much more elaborate multidimensional equilibrium model is required before analytical conclusions can be drawn.

The model finally developed considers total cost of both the sulfuric acid and power industries and chooses the set of alternatives that minimize the total cost. Sulfuric acid producers are given a choice of continuing production or buying acid from any steam plant. Steam plants not meeting SIP are given the choice of (1) selecting a clean fuels strategy, (2) selecting a calcium sludge scrubbing technology, or (3) selecting a sulfuric acid or sulfur-producing scrubbing technology. In the latter case, product would then be available to supply sulfuric acid plants if they choose to buy it. The mix of abatement strategies and marketing patterns resulting in the lowest possible cost to the combined industries (society) is said to be optimal. Economic theory also supports the proposition that such a solution simulates the result of long-run competitive equilibrium solutions.

The model implicitly ranks potential acid buyers as described earlier under The Demand Curve for Abatement Acid except that every potential abatement acid producer is given his own window through which to view the market with reference to his specific location. As the model is being solved this view is dynamically changed to reflect the bidding away of markets by other potential abatement producers. The decision making process might be viewed in two stages: (1) the steam plant is bidding for markets it might want at a given price and (2) it is deciding if it wants the market at all. The results of this bidding process interacts with the plant's abatement strategy decision. The task of simulating this process from the viewpoint of 166 acid producers and 610 steam plant boilers can be solved with modern computers and linear programming techniques. The solution reveals not only which acid producers would buy and which steam plants would sell sulfuric acid, but also which steam plants would sell to which acid plants. Any variation to this optimal solution would increase the total cost to both industries.

Analysis of the Model

Without clean air restrictions, computer runs indicate that only two sulfuric acid plants would be interested in buying 15,000 tons of abatement acid, given the March 1975 price of \$60/ton of sulfur f.o.b. Port Sulphur, but this would not support the output of even the most likely boiler. In other words, without other considerations such

as air quality control restrictions, it would not even pay the lowest cost boiler to supply the highest cost acid plant unless the cost of sulfur increased substantially.

Air pollution control restrictions are real, however, and some economic effect can be expected in meeting current and future control requirements. At present, no single available option (low-sulfur fuel, fuel desulfurization, stack gas scrubbing, etc.) appears to satisfy the needs of all power plants; therefore, the option taken can be expected to be the lowest cost one for each power plant. Based on current data paying either the premium for low-sulfur fuel or limestone scrubbing costs appears to be the lowest cost economic options. If a credit, tax, subsidy, or opportunity cost equal to these options could be absorbed at each power plant, the net effect on the price needed to justify production of abatement acid would be to lower the abatement cost curve SS' in Figure 12, thereby, increasing the equilibrium quantity of abatement acid. This could also be thought of as the revenue requirement necessary to bring supply and demand into balance at any desirable level of abatement acid production. Naturally, the "desirable level" will depend heavily on how much society is willing to pay for air pollution control.

If revenue such as a credit, market adjustment factor, penalty, or opportunity cost equal to \$50/ton acid were to be acknowledged by the power company as the cost of pollution control, net reduction on cost (price) at which abatement acid enters the market could be as much as \$50/ton. For example, a 500-MW power plant burning coal with 3.5% sulfur could produce about 112,900 tons/yr of acid by magnesia scrubbing for about \$85/ton (\$0.30/million Btu). If the lowest cost option for pollution control was limestone scrubbing at \$70/ton of acid equivalent (\$0.25/million Btu), then the acid could enter the market for as little as \$15/ton and the power plant not incur any higher costs for manufacturing acid than limestone scrubbing. Since it costs most commercial acid producers at least \$25/ton to produce, many would be interested in acid at this price.

Results from the Model

An actual run of the model is summarized in Figure 13. To conserve computer costs only sulfuric acid plants east of the Rocky Mountains were considered. Also those boilers whose sulfuric acid production costs were above \$100/ton of acid were screened out. As shown in Table 6, only 38 boilers qualify at this screening level. The system is designed so that the level of the screen can be changed easily. Note that as the level of market adjustment is parametrically increased, equilibrium quantities of abatement sulfuric acid increase.

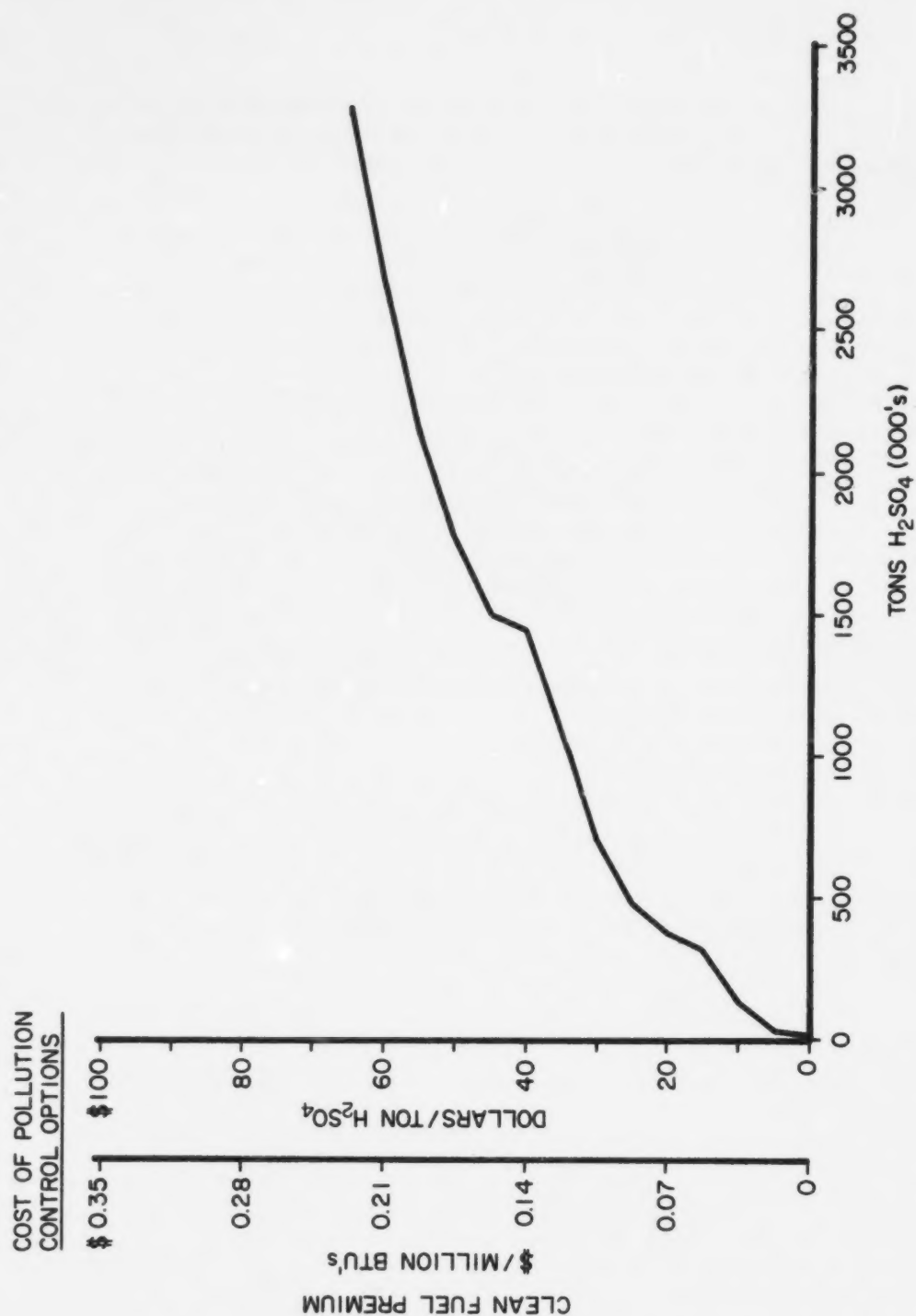


FIGURE 13 : POLLUTION CONTROL ADJUSTMENT NEEDED TO MARKET ABATEMENT H_2SO_4
(SULFUR PRICE @ \$60/TON F.O.B. PORT SULPHUR)

At a \$65/ton market adjustment, all 38 boilers would scrub to produce 3.285 million tons of abatement acid. While including more boilers might affect the upper end of this curve, the lower end would probably not change.

From an opportunity cost point of view, it was considered important to run a second case in which limestone scrubbing versus sulfuric acid were compared, since from the scrubber cost study, EPA-600/2-75-006, it was known that by ignoring market revenue the limestone throwaway system was the least-cost process. In this run, the market adjustment was raised to a maximum of \$175/ton of sulfuric acid equivalent for the limestone process so that 169 rather than 38 of the best boiler candidates could be considered. Rather than a uniform market adjustment, individual adjustments were placed on each boiler at an opportunity cost level equal to the sulfuric acid equivalent for limestone throwaway. At the current price of \$60/ton of sulfur, 7.447 million tons of sulfuric acid were produced and marketed out of the total 7.749 million tons considered. Implications of such a solution rest heavily on the assumption that retrofit difficulty for a given boiler would be similar for both processes and the level of long-run sulfur price is realistic.

Detailed listing of this particular optimal solution is not ready for publication. However, a sample computer report format outlining results of the optimal solution is presented in Table 11. A complete detailed listing of the results of analysis is provided in this table. The results could be further depicted on a map providing the geographic distribution of the power plants and the acid plants identified in the abatement production-marketing pattern for the optimal solution.

The published version will also provide a computer printout report of the optimal solution including the information outlined in Table 11.

Another Use of the Model

Another important methodological use of the marketing model is shown in Figure 14. This is the welfare econometric notion of social cost as reflected through consumer and producer surplus. Figure 14 is the classical presentation of these concepts. The argument is that the area under the demand curve DD' (DRQS) out to supply quantity Q is the total gain to consumers (acid plants) from the purchase of Q tons of sulfuric acid. (It should be recognized that marketers can't give preferential treatment to certain customers because of antitrust laws; therefore, in the optimum solution all customers pay the same price for abatement acid.) Consumers pay a total of P \$/ton times Q tons or the

Table 11. SAMPLE COMPUTER REPORT OF OPTIMAL SOLUTION

NO.	FPC CODE	BOIL	LOCATION	CAPACITY	LIMESTONE	MAGNESIUM	SODIUM	MARGIN
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
NO.	ACID PLANT	LOCATION	DEMAND	PURCHASES	PRICES	PORT SULF		
(10)	(11)	(12)	(13)	(14)	(15)	(16)		

- (1) Power plant listed in a ranked order from lowest to highest scrubbing cost (1...610 possible)
- (2) FPC power plant code
- (3) Boiler number
- (4) Power plant location
- (5) Abatement capacity (000's tons H_2SO_4)
- (6) Limestone slurry scrubbing cost, \$/ton 100% H_2SO_4 equivalent
- (7) Magnesia slurry scrubbing cost, \$/ton 100% H_2SO_4
- (8) Sodium solution scrubbing cost, \$/ton 100% H_2SO_4 equivalent
- (9) Margin represents the stability of the solution. It is the marginal increase in sulfuric acid production cost or reduction in sales revenue which could result without changing the optimal production-distribution solution.
- (10) Acid plant number (1...166 possible)
- (11) Name of acid plant buying abatement acid from the above power plant
- (12) Location of acid plant
- (13) Acid plant production capacity (000's tons)
- (14) Abatement acid purchased from steam plant (000's tons)
- (15) Abatement acid price \$/ton f.o.b. power plant
- (16) Avoidable cost of acid production using elemental sulfur at given f.o.b. Port Sulphur price.

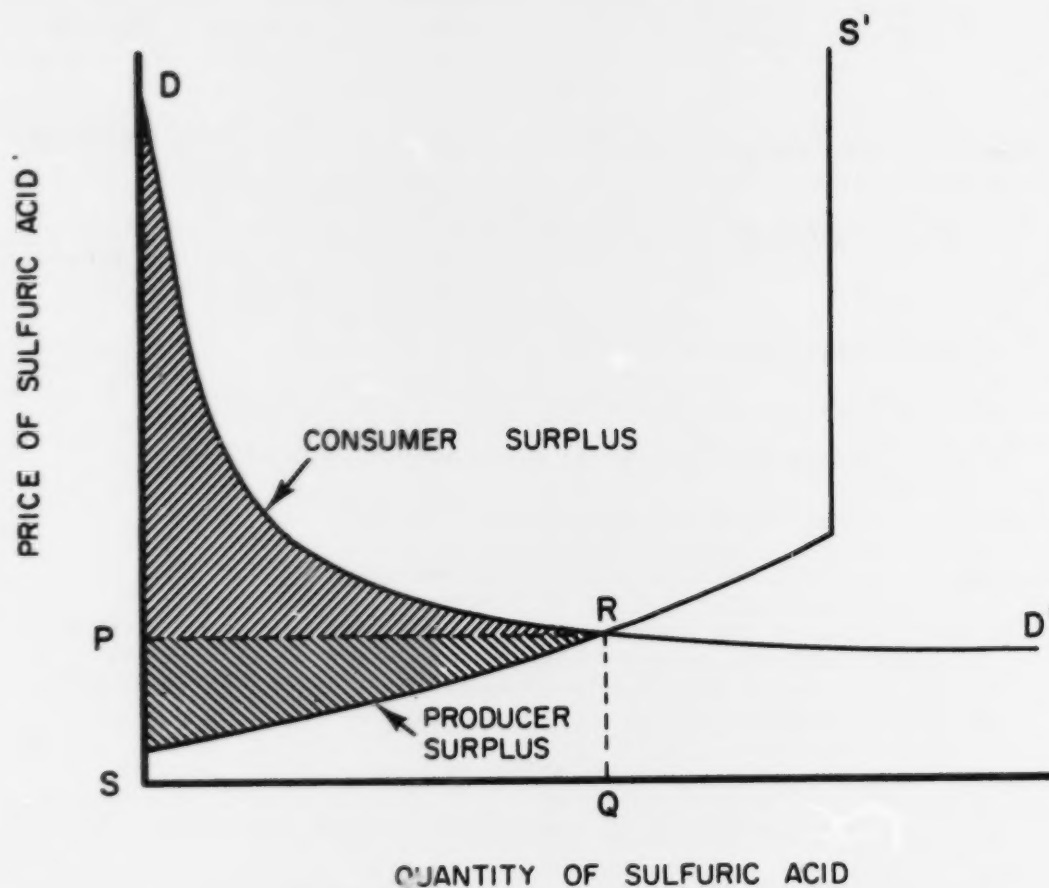


FIGURE 14: CONCEPTUAL DEMAND CURVE FOR SULFURIC ACID AND SUPPLY CURVE FOR ABATEMENT PRODUCTION, ILLUSTRATING PRODUCERS & CONSUMERS SURPLUS.

rectangle below P out to Q (PSQR). Consumer surplus is the difference or the indicated area (DPR) in Figure 14. Similarly this same total revenue goes to producing power plants whose total is the area (RSQ) below the supply curve SS' out to supply quantity Q. Producer surplus is the area below P and above the supply curve, as indicated (PRS). Net social gain, therefore, is the combination of consumer and producer surplus. At equilibrium the most marginal consumer and producer neither gain nor lose, but all others in the solution are better off. Net social gain is the amount by which they are better off. Methodology used in this study does not address specific division of net social gain between producer and consumer. It is assumed this will be determined in the market place.

With the above welfare econometric notions as background, consider their operational interpretation in terms of the present model. For example, with a parametric market adjustment of \$65/ton of H_2SO_4 , total cost of acid production in both industries is \$1.347 billion and the cost to power consumers for the market adjustment on 3.286 million tons of acid is \$214 million (about 2.5 mills/kWh to the customers served by the 38 subject boilers). The level of this market adjustment is very important politically since this is the apparent change in cost of power for resolving about 65% of their total excess SO_x emission problem. However, the cost to both industries (really the sulfuric acid industry) before the adjustment was \$1.418 billion, so that total cost reduction of the combined industries is \$71 million. Hence, the real cost to society is only \$143 million, with \$71 million being the combination of consumer and producer surplus.

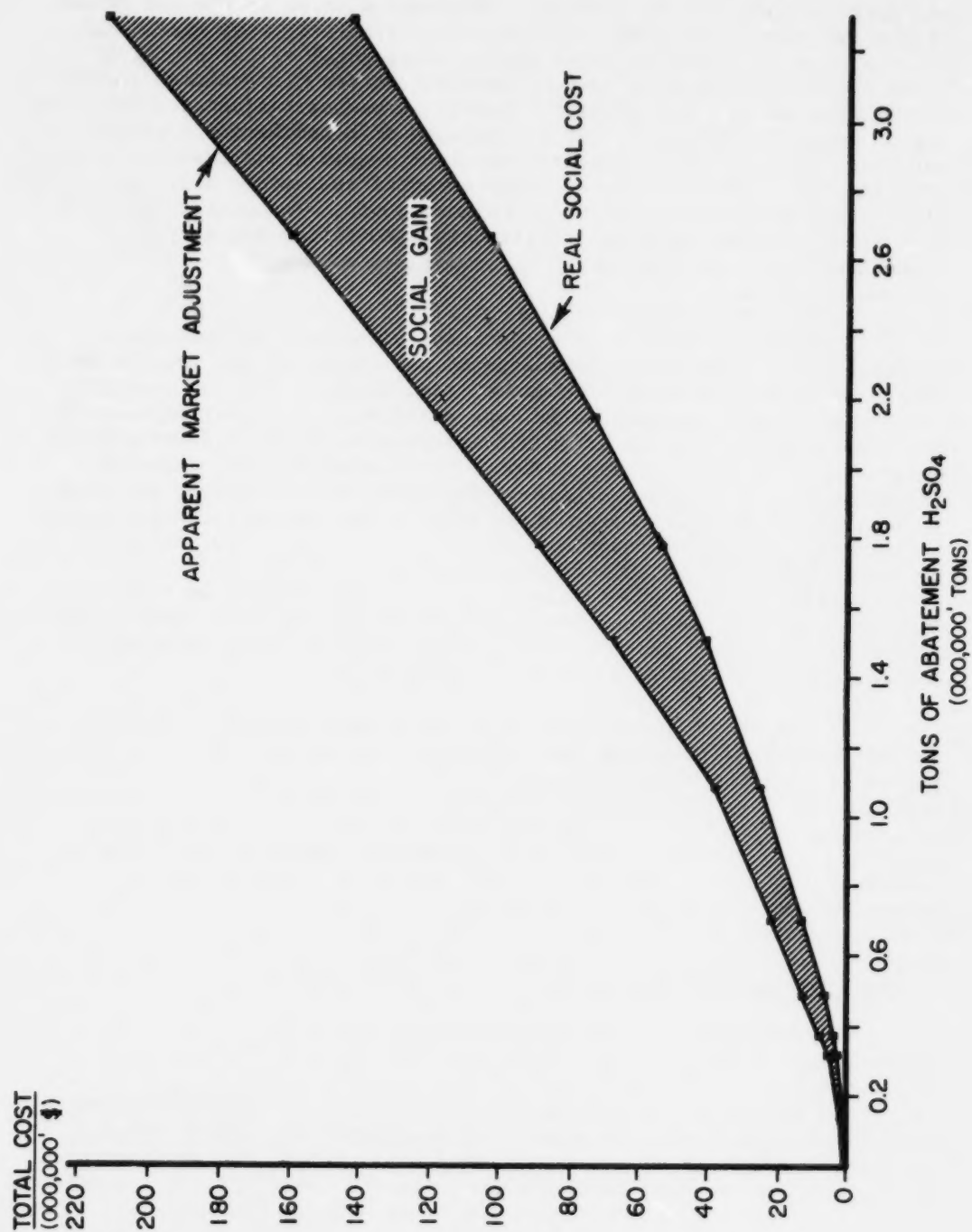
The divergence between apparent market adjustment and real social cost for eliminating specific levels of SO_x emissions is shown in Figure 15. This welfare econometric phenomenon is significant since it is a readily overlooked aspect relating to the methodology of economic comparisons of saleable versus throwaway abatement strategies. It supports one's intuitive resource conservation feelings and becomes more socially significant in the face of long-term Frasch sulfur supply shortages and higher prices.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The point has been passed where studies about hypothetical plants and markets are relevant in environmental and energy related research. Important decisions are being made which involve substantial financial commitments. Decision makers at the power utility and national

Figure 15: SOCIAL COST OF ABATEMENT BY-PRODUCT H_2SO_4 PRODUCTION.



policy level need the best possible information on which to base these decisions.

Recognizing this need, a systems approach to potential abatement production and marketing of byproduct elemental sulfur and sulfuric acid in the U.S. was taken. It was concluded in this research phase that adequate data bases do exist. However acquiring, organizing, verifying, and updating them is still a significant problem to be resolved. A market simulation model was developed to use these data bases which permit the evaluation of alternative production and marketing strategies.

The system was used to make trial runs to (1) demonstrate its validity and (2) pretest the approach to analysis as well as presentation of results. The philosophy was that agreement should be reached on methods of analysis before spending large sums on computer runs. Also, final runs should be made as close to publication date as possible since the data bases and policy considerations are so dynamic. However, some preliminary conclusions can be drawn based on the trial runs subject to the specific assumptions made, and the degree to which simulations based on 1972 production data can be extrapolated to future conditions.

Total potential abatement acid production based on total emissions east of the Rocky Mountains in 1972 was 22.3 million tons from 2,564 boilers. Total acid consumption for the same area, excluding existing abatement production, was slightly higher. Hence, total potential abatement production could have been physically absorbed. The purpose of the market simulation model is to estimate how much would have been supplied in a competitive market environment; who would produce it, and who would consume it.

Based on SIP requirements in March 1975, only 610 of these boilers were out of compliance, representing 9.7 million tons of potential abatement acid. Of these, 70% were more than 15 yr old, indicating unfavorable scrubbing economics. Many of these boilers had very high abatement costs while only a few new large boilers had reasonable costs. A point is obviously reached where an alternative such as clean fuel substitution is less costly than scrubbing.

While the level of alternative emissions control cost other than scrubbing is outside the scope of this study, it was analyzed parametrically to determine its impact on simulated equilibrium quantities of abatement acid supply and demand. At zero alternative cost there was no significant power plant production. It can therefore be concluded that when sulfur value is \$60/ton there would be no power plant production without regulations for emission control. As plants are forced to take some action, the cost for alternative controls can be considered as a credit to recovery processes and provides the

basis for assigning a sulfuric acid market adjustment value. At the highest level of market adjustment analyzed, \$65/ton H_2SO_4 (23¢/million Btu), 38 boilers producing 3.3 million tons were in the equilibrium solution. Definite conclusions cannot be drawn from this analysis without an insight into the clean-fuel market situation, which is uncertain at this time.

Conclusions must also be tempered with expected sulfur price levels, which could fluctuate in the short run but may stabilize at relatively high prices depending on energy costs and the severity of the impending Frasch sulfur shortage.

For boilers that do not select an alternative strategy, such as clean fuel substitution, the question remains as to whether they would produce (1) sulfuric acid, (2) sulfur, or (3) a throwaway sludge. While the sulfur alternative was modeled, production costs with current technology were high enough that the alternative did not require a computer run to conclude that sulfur would not be chosen over acid at any boiler. But if technology improves, sulfur should be subjected to closer analysis by the model because of the potential savings in freight and storage costs for sulfur over acid.

The throwaway sludge alternative was analyzed in detail since it is the lowest cost scrubbing method. In this case marketing revenue would have to exceed the cost differential for a given boiler before acid production would be selected. For this analysis only boilers with cost less than \$175/ton of H_2SO_4 (61¢/million Btu) were analyzed; it is recognized that this level is possibly high, but it was chosen to study the market for large quantities of acid. Those having alternative costs higher than this would definitely not choose a scrubbing technology. In competition with acid produced from \$60/ton sulfur, 7.4 million tons of acid (96% of the total considered) were produced in lieu of sludge. Conclusions based on this result are less dependent on retrofit difficulty inaccuracies than a clean fuel alternative but are dependent on sulfur price. This result should be analyzed in future runs at alternate price levels.

An important finding was that while long-run competitive equilibrium solutions predict what may happen in competitive markets, they do not identify net social gain. For example, with a \$65/ton market adjustment value for sulfuric acid, total adjustment is \$214 million/yr. However, \$71 million of this was identified as savings to the utility (producer surplus) and acid industries (consumer surplus), though it is not possible to identify exactly who would benefit and by how much. Society in general would gain, however, which is not the case with a throwaway strategy.

Although the trial results thus far are very preliminary, they offer considerable encouragement that a significant amount of by-product sulfuric acid could be moved within the present market structure at a sales value high enough to make sulfuric acid FGD processes competitive with throwaway sludge systems.

Specific conclusions at this preliminary stage should be drawn with caution. Publication of the detailed analysis is delayed to accommodate further refinement and updating of data bases. For example, several boilers that required control in the data base are now in compliance with regulations. Furthermore, Indiana and Ohio SIP were in litigation and boilers in these states were not considered as scrubbing candidates. However, the results to date indicate that marketing sulfuric acid from more efficient boilers is a viable alternative.

Recommendations

Although the market simulation model outlined above is workable and has been demonstrated as a highly effective way to address the air pollution abatement problem, it needs further updating, verification, and refinement before it can be used as an accurate decision making tool. It is recommended that emphasis in the future should be placed first on improving the existing data bases which support the systems analysis approach to the evaluation of potential byproduct marketing of various FGD abatement products in the 48 contiguous states of the U.S. Then the elemental sulfur and acid markets can be accurately assessed, and other abatement byproducts such as $(\text{NH}_4)_2\text{SO}_4$, CaSO_4 , NaSO_4 , etc., can be considered. When finally developed, the data bases and the model would be available on a time-sharing network accessible by any private or public agency interested in abatement byproduct marketing.

Four major areas need further refinement and verification:

1. The scrubbing cost generator.
 - a. Include scrubber system retrofit difficulty factors for specific power plants in the U.S.
 - b. Update the SIP standards for power plants in the U.S.
 - c. To derive more representative power plant operating data, expand the 1972 FPC Form 67 master file for operating characteristics of existing power plants in the U.S. to include 1969, 1970, 1971, and 1973 data, as well as new plant projections for 1978 and 1983.

- d. Convert the FPC master file to the System 2000 data management system for all years outlined in c above.
 - e. Refine FGD cost generation model to accommodate economies to scale for plants with more than one boiler selected for scrubbing.
- 2. Update and verify the production cost generator for sulfuric acid and elemental sulfur, including tail gas cleanup for new and existing plants.
 - 3. The transportation-storage cost generator.
 - a. Update the transportation cost generator to include current rates on rail, barge, and truck shipments.
 - b. Update the elemental sulfur transportation, terminal storage, and delivery cost to acid plants.
 - 4. Develop projections for 1978 power plant abatement production estimates, commercial acid production, sulfur-supply, and define other byproduct supplies of recovered sulfur and byproduct acid.

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15. Short Line Rail Mileage published by all railroads operating east of the trans-continental territory in Figure 10.

APPENDIX A

GENERAL CONVERSION FACTORS

EPA policy is to express all measurements in Agency documents in metric units. Values in this report are given in British units for the convenience of engineers and other scientists accustomed to using the British system.

The following conversion factors may be used to provide metric equivalents.

CONVERSION FACTORS FOR METRIC EQUIVALENTS OF BRITISH UNITS

	British		Metric	
	Multiply	By	To obtain	
ac	acre	0.405	hectare	ha
bbl	barrels of oil	158.97	liters	l
Btu	British Thermal Unit	252	gram-calories	g-cal
° F	degrees Fahrenheit-32	0.5555	degrees Centigrade	° C
ft	feet	30.48	centimeters	cm
ft ²	square feet	0.0929	square meters	m ²
ft ³	cubic feet	0.02832	cubic meters	m ³
ft/min	feet per minute	0.508	centimeters per second	cm/sec
ft ³ /min	cubic feet per minute	0.000472	cubic meters per second	m ³ /sec
gal	gallons	3.785	liters	l
gpm	gallons per minute	0.06308	liters per second	l/sec
gr	grains (troy)	0.0648	grams	g
gr/ft ³	grains per cubic foot	2.288	grams per cubic meters	g/m ³
hp	horsepower	0.7457	kilowatts	kW
in	inches	2.54	centimeters	cm
lb	pounds	0.4536	kilograms	kg
lb/ft ³	pounds per cubic foot	16.02	kilograms per cubic meter	kg/m ³
lb/hr	pounds per hour	0.126	grams per second	g/sec
mi	miles	1609.	meters	m
rpm	revolutions per minute	0.1047	radians per second	rad/sec
scfm	standard cubic feet per minute (32° F)	1.695	normal cubic meters per hour (0° C)	Nm ³ /hr
ton	tons (short) ^a	0.90718	metric tons	t
ton, long	tons (long) ^a	1.016	metric tons	t
ton/hr	tons per hour	0.252	kilograms per second	kg/sec

^aAll tons are expressed in short tons in this report except sulfur which is expressed in long tons.

REGENERABLE PROCESSES SESSION

Chairman: Richard D. Stern
Chief, Process Technology Branch
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

STATUS OF DEMONSTRATION OF THE WELLMAN-LORD/ALLIED
FGD SYSTEM AT NIPSCO'S D. H. MITCHELL GENERATING STATION

PART I

BACKGROUND AND OVERVIEW

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Northern Indiana Public Service Company
Michigan City, Indiana

Roger C. Christman

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ABSTRACT

In June of 1972, the Northern Indiana Public Service Company and the U. S. Environmental Protection Agency entered into a cost-shared contract for the construction and operation of a flue gas desulfurization demonstration plant. The system selected for the project was a combination of two processes which had been installed and operated in applications other than coal-fired utility boilers. These are the Wellman-Lord SO₂ Recovery Process and the Allied Chemical SO₂ Reduction Process. Used in tandem, the two processes result in a regenerable FGD process which recovers SO₂ as marketable elemental sulfur. The Wellman-Lord/Allied FGD system has been installed on NIPSCO's 115MW coal-fired Unit No. 11 at the D. H. Mitchell Station in Gary, Indiana.

The construction of the demonstration plant is essentially complete with mechanical checkout underway. During the coming year the system will be operated by Allied Chemical Corporation. The EPA has retained the services of TRW's Environmental Engineering Division to conduct a comprehensive test and evaluation of the Wellman-Lord/Allied demonstration plant. A final project report, to be prepared by TRW, will include information on the pollution control performance, secondary effects, economics and reliability of the system. It is anticipated that the NIPSCO/EPA demonstration project will provide information useful to the continuing evaluation of alternatives in dealing with air pollution problems.

PART I

BACKGROUND AND OVERVIEW

Northern Indiana Public Service Company is a combined natural gas and electric utility operating in the northern third of Indiana. The service area includes the highly industrialized and environmentally sensitive southern tip of Lake Michigan. The Company operates three coal-fired generating stations along the lake shore and one of these, the D. H. Mitchell Station in Gary, was selected by NIPSCO as a site for demonstration of a flue gas cleaning process.

In the early 1970's the Company was involved in evaluating alternatives for dealing with the SO₂ problem and the regulations established by the Federal EPA and state and local authorities. In considering flue gas desulfurization it was necessary to examine both the ability to meet SO₂ emission requirements and the total environmental impact of the system. Limited availability and high cost of land in the immediate area of the NIPSCO plants meant that the installation of a throw-away system would involve the overland hauling of the sludge product for substantial distances. As a result, the Company's attention focused on regenerable processes which produced sulfuric acid or elemental sulfur suitable for disposal by sale.

Simultaneous with NIPSCO's evaluation of FGD alternatives, the Industrial Environmental Research Laboratory - RTP of the U. S. Environmental Protection Agency was also evaluating regenerable processes for possible demonstration at the 100MW level. The EPA, having two demonstration projects underway which involved the production of sulfuric acid, was seeking an FGD process capable of producing marketable elemental sulfur. Among the candidate processes, the Wellman-Lord SO₂ Recovery Process (developed and marketed by Davy Powergas of Lakeland, Florida) appeared to be the most fully developed with a 70MW oil-fired boiler application operating in Japan. Allied Chemical had demonstrated a process for reduction of SO₂ to elemental sulfur. This plant, installed on a non-ferrous smelter in Ontario, had a sulfur throughput rate which was several-fold greater than the system subsequently constructed at NIPSCO. All indications pointed to the fact that the Allied SO₂ Reduction Process could be mated to the Wellman-Lord SO₂ Recovery Process, thus resulting in a regenerable FGD process with elemental sulfur as the major product.

The parallel interests of NIPSCO and EPA in the Wellman-Lord Process led to initiation of negotiations involving EPA, Davy Powergas, Allied Chemical Corporation, and NIPSCO early in 1972. The EPA and NIPSCO reached agreement on a cost-shared contract in June 1972. The EPA-NIPSCO contract and, in turn, the NIPSCO-Davy Powergas contract has requirements for an emission control system which will operate at a minimum of 90% SO₂ removal from the flue gases of the 115MW boiler firing coal and with a sulfur content of 3.5%. The process also is guaranteed not to allow any emission in excess of 200 ppm by volume of SO₂ in the exit gas with lower sulfur fuel. An existing electrostatic precipitator is expected to reduce the dust loading to 0.044 grains per actual cubic

foot at the scrubber inlet. The Davy Powergas system has been designed with a pre-scrubber to remove 0.2 grains per ACF with the capability of handling considerably greater fly ash loadings for short periods. Ash content of the Midwest coal is approximately 10% and the heat content is 11,000 BTU per pound.

The descriptions of the Wellman-Lord and Allied Chemical processes are well reported elsewhere and will not be covered here. The current status of the project is discussed below.

Construction of the plant began in the Fall of 1974, with pilings and foundations completed in December of that year. The field activity was suspended during the winter months except for receiving and off-loading of equipment. Equipment delivery problems which were typical of the construction industry in 1974 threatened to drastically delay completion of the project. These difficulties relaxed somewhat in late 1974 as the business slump intensified and the construction proceeded in a fairly orderly fashion through 1975. At this writing, the construction is essentially complete except for minor painting and insulation. Mechanical checkout of equipment is underway and it is anticipated that flue gas will be admitted to the absorber in April of 1976. The procedures and timing of startup activities are discussed by Allied Chemical in Part II of this paper.

In order to evaluate the performance and economics of the Wellman-Lord/Allied demonstration plant, the Industrial Environmental Research Laboratory - RTP retained the services of TRW's Environmental Engineering Division. The TRW activities include: the conduct of a baseline test of the host boiler prior to installation of the FGD system (completed); conduct of an acceptance test to determine if contract guarantees have been met; and conduct of a one-year demonstration test during which time the long-term performance and economics data will be collected and evaluated for presentation in a final report. In preparation for the acceptance and one-year demonstration test efforts, TRW has designed and installed an automated test measurements system which includes simultaneous measurement and recording of both host boiler data and FGD system performance data. The continuous measurements will be checked and supplemented by periodic manual sampling tests. The continuous monitoring and automatic data acquisition permits correlation of FGD performance with changes and rates of change of host boiler operating conditions. It will also be possible to evaluate the FGD system emission response to changes in operating mode resulting from optimization efforts by the Allied Chemical operating staff. The final project report to be prepared by TRW will include data for and assessment of the pollution control performance and secondary effects of the system, evaluation of the system reliability and economics, discussion of the system's response to transient conditions (boiler startup, shutdown, load changes, fuel changes, etc.), and an evaluation of the range of utility population applicability of the Wellman-Lord/Allied FGD system. Data and information for the final report will be supplied by NIPSCO and Allied Chemical in addition to the data collected by the TRW operated test measurements system.

The projected cost of the demonstration system is shown on Table I. Calculations were done on the basis of complete financing by NIPSCO although approximately 50% of capital costs were actually covered by Federal funds.

The costs presented are for a 115MW retrofit system. Costs for full-scale or new systems would, of course, benefit from some economy of scale.

The Company is hopeful that the information and data which will be developed in the coming year as a result of operation of this important FGD demonstration system will be helpful in evaluating SO₂ alternatives for NIPSCO and the utility industry in general. The Wellman-Lord/Allied demonstration represents only one route under investigation by NIPSCO. At the present time, the SO₂ regulations require that the D. H. Mitchell Station comply with the emission limitation of 1.2 pounds SO₂ per million BTU. The four coal fired units, totaling approximately 500MW gross, have been burning Western coal for a little over 12 months. The station is in SO₂ emission compliance. Marked loss in precipitator efficiency has been noted. Also, ash hopper overflows and fly ash sluice piping systems are being plugged frequently with deposits. Coal feed to the 115MW demonstration unit will change from Western coal to Indiana-Illinois coal during the demonstration year, while the other three units will remain on the Western coal. This should permit some interesting comparisons of operating and maintenance requirements.

SO₂ emission regulations in the State of Indiana have not yet jelled. At present, NIPSCO's two other coal fired stations are using 3% sulfur coal. A new coal fired station now under construction with a 500+ MW cyclone unit and a 500+ MW pulverized unit are to be fired with Western coal to attain emission limitation of 1.2 pounds SO₂ per million BTU. Northern Indiana Public Service Company is cognizant of the difficulties experienced by others in SO₂ scrubbing. This soon will be supplemented by more intimate experience. The same comment applies to use of low sulfur coal. The course which NIPSCO takes to satisfy SO₂ regulations is not expected to be a highway, rather a path certainly not well defined at this time. Future action, if required, will be site related, based on experience and economic evaluation.

TABLE I

<u>Capitalization (1976 dollars)</u>	
Including top charges ⁽¹⁾ (\$129 per installed KW)	\$14,824,690
Excluding top charges	\$12,794,733
<u>Operating Cost (After Demonstration Year)</u>	
Operation and Maintenance ⁽²⁾	\$ 2,513,000
Product Credits, sulfur at \$32/long ton purge salts at \$50/ton	(361,560)
Net Operating Cost	\$ 2,151,440
<u>Fixed Charges</u> ⁽³⁾ (26% x \$14,824,690)	\$ 3,854,419
<u>Total Annual Cost</u>	\$ 6,005,859
<u>Total Annualized Cost</u> ⁽⁴⁾	8.1 mils/KWH

Notes:

- (1) Interest during construction, overhead.
- (2) Operating supplies include \$400/day for anti-oxidant agent or \$11,200/month. Early operation may show anti-oxidant is unnecessary or needed in lesser amounts.
- (3) Plant life of 10-15 years assumed.
- (4) Annual load factor of 73.5% assumed.

STATUS OF DEMONSTRATION
WELLMAN-LORD/ALLIED CHEMICAL FGD SYSTEMS
NIPSCO D. H. MITCHELL GENERATING STATION

PART II

CURRENT STATUS & OPERATING PLAN

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ABSTRACT

Construction of the SO₂ emission control facility at NIPSCO is nearing completion and preparations for operation are now well underway. Start-up specialists of Allied Chemical and Davy Powergas are presently working with Allied's permanent operating staff in completing mechanical checkout and acceptance of the plant.

Following completion of a stringent 15 1/2 day performance test program, operation of the facility for a demonstration period of about one year's duration will be conducted to document the operating efficiency and reliability of the FGD system over a wide range of boiler operating conditions. Allied Chemical will operate the FGD system for NIPSCO on a continuing basis and will market the elemental sulfur and sodium salt products.

Status of Demonstration of Wellman-Lord/Allied Chemical
FGD Systems at NIPSCO D. H. Mitchell Generating Station

Part II: Current Status & Operating Plan

The engineering and construction phases of the SO₂ emission control project at Northern Indiana Public Service Company's (NIPSCO) D. H. Mitchell Station, Gary, Indiana will be completed this month. Preparations for start-up and operation of the system are now well advanced.

The flue gas desulfurization (FGD) system which has been installed is an integration of the Wellman-Lord SO₂ Recovery Process of Davy Powergas (DPG) and Allied Chemical's SO₂ Reduction to Sulfur. DPG is the engineer and constructor of the entire facility while Allied Chemical will operate the complete system and market the products.

Several "firsts" are represented by this venture. It will be the first regenerable FGD system to control the total flue gas emission from a full-scale coal-fired generating unit, as well as the first application of the Wellman-Lord process on a coal-fired boiler. It will be the first FGD system to recover elemental sulfur commercially from the flue gas emission of an electric utility. It is also the first time that a utility has engaged a chemical company to operate and maintain the emission control facility and to market the chemical products.

Participation in this project by Allied Chemical is a logical extension of pollution control services that Allied has provided to others for many years as part of its sulfuric acid and sulfur products operations and sales in the U.S. and Canada. Such activities include control of SO₂ emissions from metallurgical operations and reprocessing of waste acids from petroleum refineries and other sources. The skills and experience that are an integral part of Allied's own operations are now being applied to the chemical process problem of SO₂ emission from an electric utility.

Experience gained in chemical plant start-ups over the years has led to the belief in Allied that there are two key elements in the successful start-up of any plant, whether it be a new process or a new installation of an old, well established process. These are:

- technology which provides a sound basis for the process and equipment design, and
- an experienced operating staff, technically oriented to the specific requirements of the chemical process.

These elements are equally important. Success cannot be assured with either one alone. It has been Allied's objective to incorporate both into the NIPSCO project.

At the inception of this project, NIPSCO commissioned Allied to provide the following services:

- Preoperational Activities
- Mechanical Checkout and Acceptance
- Start-up & Performance Testing
- Demonstration Period Operation
- Continuing FGD System Management

PREOPERATIONAL ACTIVITIES

The NIPSCO preoperational effort has been conceived and carried out on the basis that the facility will be a long term operation and that Allied will have continuing responsibility for its management. The supervisors, especially selected from within Allied's organization for this project, bring to their permanent assignments at the NIPSCO facility many years of experience, not only in start-ups, but in the continuing administration and technical supervision of chemical plant operations and maintenance. Operators and mechanics, recruited locally as Allied employees, have just completed a formal training program, and training of technicians in analytical procedures is now in progress.

Other prestart-up preparations now completed include a risk analysis of each equipment item in the facility which enabled Allied Chemical to procure for NIPSCO the essential spare parts and operating supplies required to minimize down-time and maintenance costs during start-up and continuing operations. This initial provisioning is a type of insurance vital to early completion of the start-up and achievement of operating reliability.

MECHANICAL CHECKOUT & ACCEPTANCE

Allied's primary concern in this phase of the project has been to assure the operability of the plant. Much of the activity of the operating supervisors has involved inspection and monitoring of construction, with the assistance of chemical, mechanical and instrument specialists from the home office.

Conditional acceptance of the plant by Allied Chemical for NIPSCO precedes the actual start-up. Acceptance is conditional at this point because certain items of rotating equipment, such as pumps, blowers and agitators can only be checked under actual process conditions. The plant will be accepted in its entirety at such time as all of the equipment is functioning properly.

START-UP AND PERFORMANCE TESTING

Overall direction of the operation through start-up and completion of performance testing is the responsibility of Davy Powergas, the engineer/constructor. Allied will assist DPG in conducting the performance test program established for the facility. Performance criteria for the plant are summarized as follows:

- (1) The test period will consist of 12 days' operation at an average load of 92 megawatts followed by 3½ days at an average load of 110 megawatts. Coal with an average sulfur content of 3.2% has been stockpiled for consumption during this test period.

(2) Other performance criteria provide that:

- (a) When operated with 3.15 to 3.5% sulfur in the coal, the system must achieve 90% sulfur removal from the flue gas, or retain not more than 200 ppm of SO₂ in the exit gas stream, whichever is lower. With fuels containing more than 3.5% sulfur, the absorber must achieve at least 90% sulfur removal from the flue gas. With fuels containing less than 3.15% sulfur, the absorber exit gas must contain not more than 200 ppm SO₂.
- (b) Sulfur recovery efficiency must be not less than 90% across the SO₂ reduction system, and the elemental sulfur recovered from the concentrated SO₂ must be of a quality suitable for conversion to sulfuric acid in standard sulfuric acid plants.
- (c) Aggregate consumption of utilities --- electric power, steam, cooling water and natural gas --- has been established at a fixed total maximum value.
- (d) The maximum allowable consumption of soda ash, the principal chemical raw material and a function of sodium sulfite oxidation in the absorption system, is also specified for operation at the 92 megawatt rate.

In addition to the tests that will be performed by Allied during performance testing, the operation will also be monitored by TRW, Inc. under contract to the Environmental Protection Agency.

The start-up supervisors and specialists that Allied Chemical and DPG now have on site preparing for initial operation will remain through completion of performance testing, working with the permanent Allied supervisory and hourly staff. The entire start-up organization is illustrated in Exhibit 1.

DEMONSTRATION PERIOD OPERATION

Following completion of the performance testing and final acceptance of the plant, the supervisory and technical staff will be reduced to ten people while the operation continues for a demonstration period of approximately one year's duration. The organization during this phase of the project is shown in Exhibit 2, attached.

A series of operational tests will be conducted throughout this period and the detailed data will be continuously evaluated to enable adjustments to assure the efficient performance of both the Wellman-Lord and Allied Chemical processes under changing load and other conditions.

TRW will perform periodic tests to acquire data on the operation of NIPSCO Unit 11 and to determine efficiency of particulate and SO₂ removal from the flue gas in the Wellman-Lord absorption system. Tests will be carried out over a range of boiler operating rates and conditions to document the turndown and maximum operating capabilities of the complete FGD system. Additional tests employing coals of different sulfur contents may also be conducted. The extensive information which will be developed during the demonstration period will enable projection of meaningful capital and operating costs for new and retrofit utility applications.

CONTINUING FGD SYSTEM MANAGEMENT

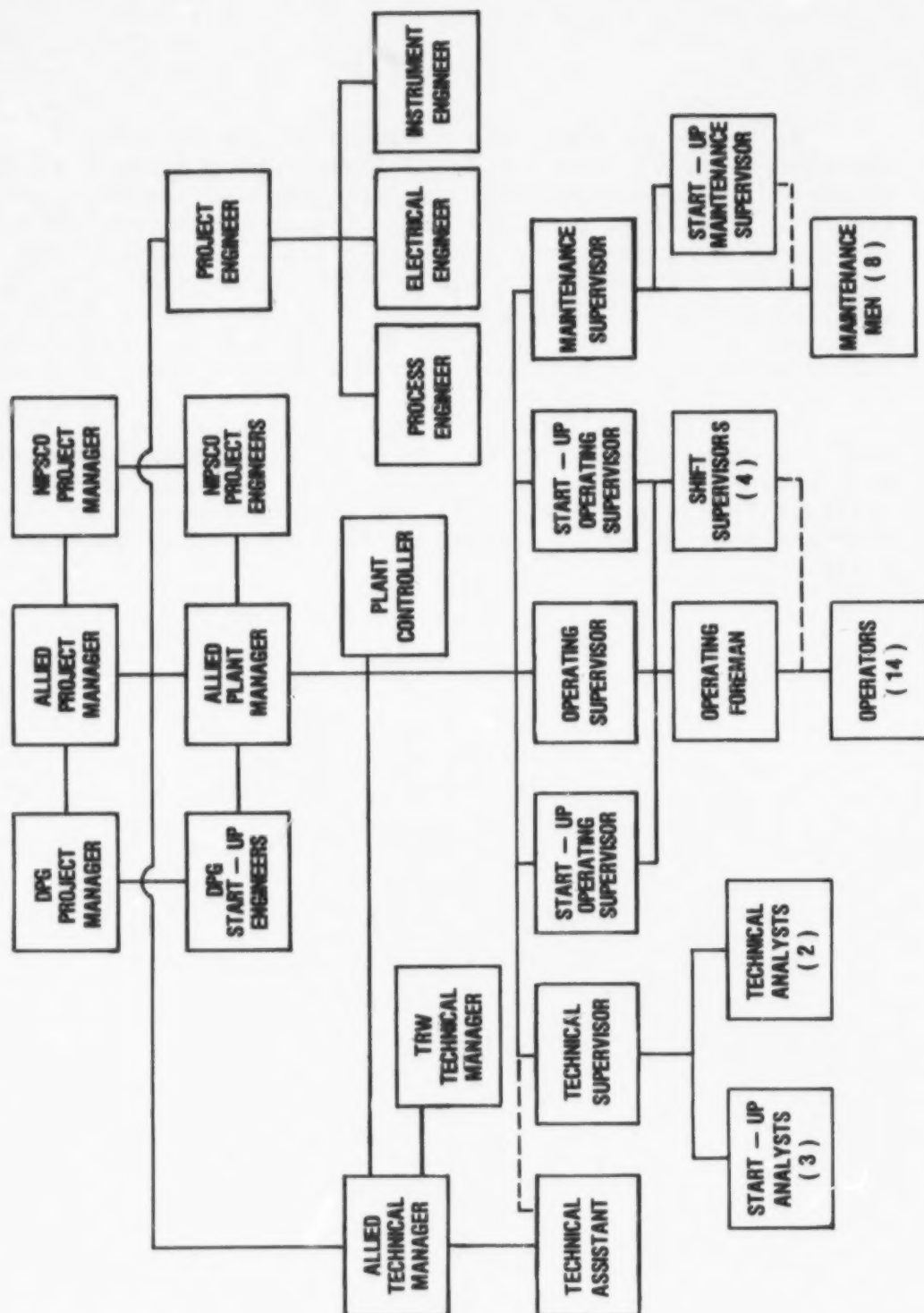
Following a decision by NIPSCO to extend operation of the SO₂ emission control facility beyond the demonstration period, Allied will perform FGD system management services for Unit 11 at the Mitchell Station on a continuing basis. The NIPSCO FGD facility will be afforded the administrative and technical support that is provided by Allied to its own national network of chemical operations. At that time, the supervisory and technical personnel will be further reduced to 8 with the staff of operators and mechanics remaining unchanged in number. Personnel for the permanent operation are shown in Exhibit 3. It is important to note that this same staff, with some additional maintenance personnel, would have the ability to operate and maintain a FGD facility serving all four coal-fired generating units at Mitchell Station.

Marketing of chemicals produced in the facility is the responsibility of Allied Chemical. The elemental sulfur product will be shipped from the site in tank trucks as a liquid. It will be consumed initially at an Allied Chemical plant in the manufacture of sulfuric acid. Likewise, the sodium salt recovered from the Wellman-Lord system as a dry granular product will be channeled into appropriate markets, primarily in the pulp and paper industry. NIPSCO will receive full credit for the revenues from the sale of these products.

In conclusion, as NIPSCO approaches start-up of the FGD facility at Mitchell Station, there is every expectation that this regenerable system will demonstrate the efficiency and reliability sought by the electric utility industry in coping with the problem of SO₂ emissions from coal-fired generating units.

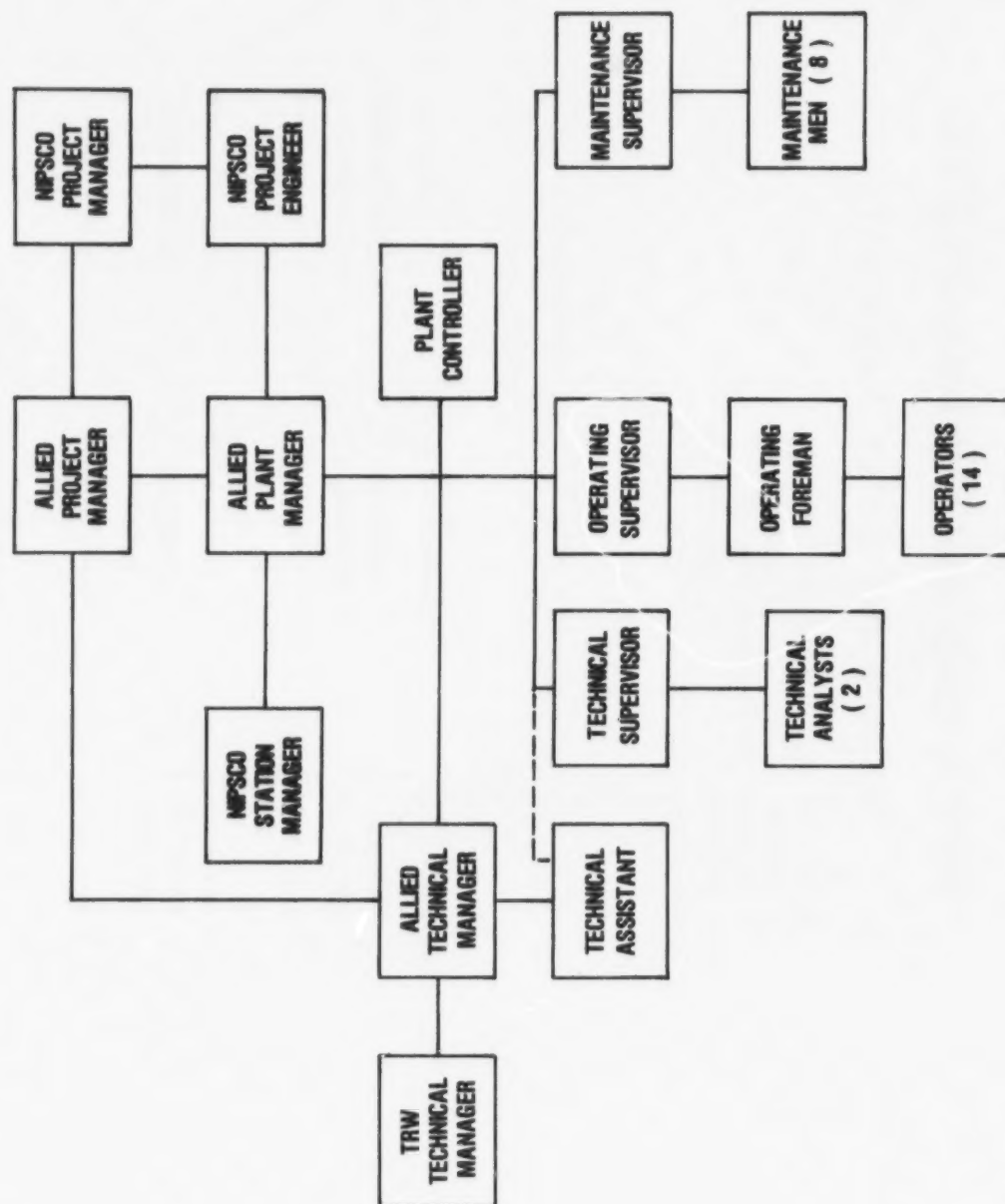
NIPSCO EMISSION CONTROL SYSTEM

Start-Up and Performance Testing



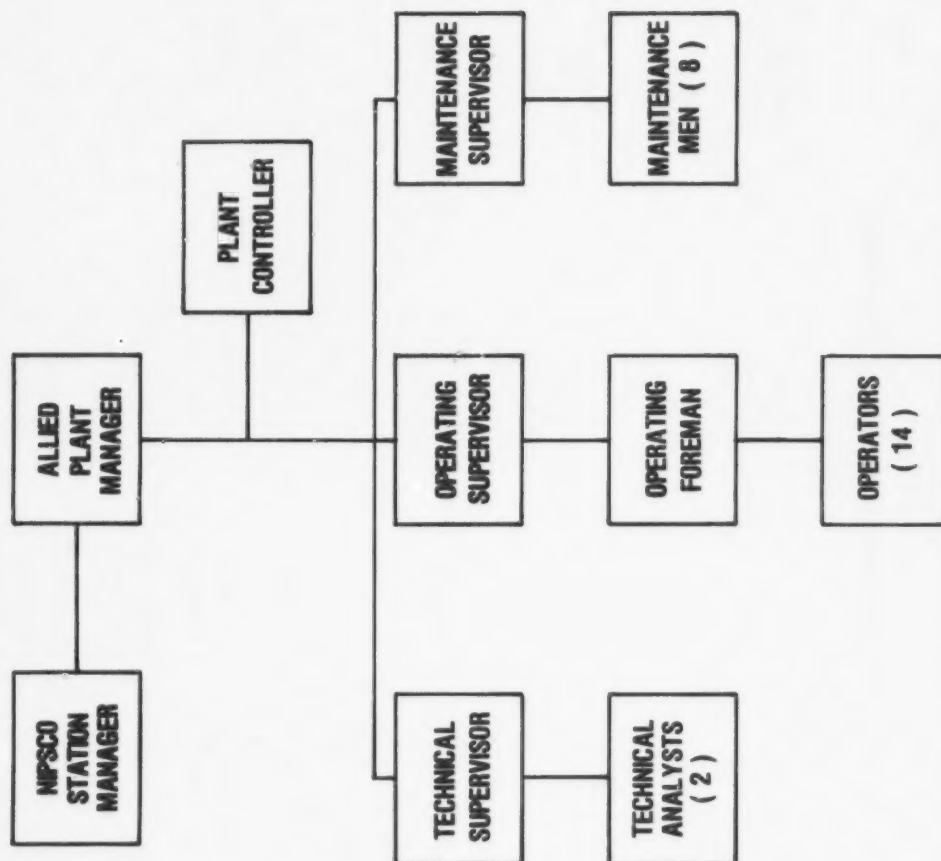
NIPSCO EMISSION CONTROL SYSTEM

Demonstration Period Operation



NIPSCO EMISSION CONTROL SYSTEM

Continuing FGD System Management



AN UPDATE OF THE WELLMAN-LORD
FLUE GAS DESULFURIZATION PROCESS

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ABSTRACT

The Wellman-Lord SO₂ Recovery Process and three different end product plants for handling the recovered SO₂ are described. A world-wide listing of all Wellman-Lord installations in operation or in the design or construction phase is given, and the performance or design of some installations is described. Capital and operating costs for a typical Wellman-Lord installation are presented, and major design criteria and their impact on cost are discussed. Problems facing the Wellman-Lord Process and action being taken to resolve them are discussed.

AN UPDATE OF THE WELLMAN-LORD FLUE GAS DESULFURIZATION PROCESS

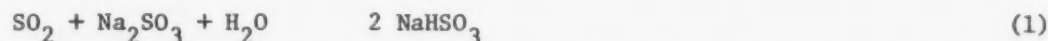
INTRODUCTION

The Wellman-Lord SO₂ Recovery Process was developed by Davy Powergas in the late 1960's. It is being used in, or designed or constructed for, thirty commercial installations throughout the world. At every installation, the Process has proven itself as operationally reliable, and has met or surpassed governmental regulations regarding SO₂ emissions.

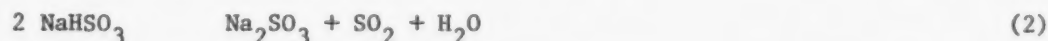
The Process can be applied to any flue gas containing SO₂. It is equally applicable to the flue gas from fossil fuel fired boilers, nonferrous smelters, sulfuric acid plants, and Claus plants. The Process uses a recycle system and yields an SO₂ gas suitable for conversion to sulfuric acid, elemental sulfur, or liquid SO₂.

CHEMISTRY

The Process is based on the chemistry of the sodium sulfite/bisulfite system. Flue gas containing SO₂ is scrubbed with a sodium sulfite solution which absorbs SO₂, converting sodium sulfite to sodium bisulfite:



The sodium bisulfite solution is regenerated by thermal decomposition. Application of heat simply reverses equation 1:



The SO₂ is recovered in a concentrated stream.

PROCESS DESCRIPTION

Gas Pre-Treatment

Each plant's pre-treatment requirements must be studied individually. For example, the flue gas from a fossil fuel fired boiler will require cooling and particulate removal prior to absorption of the SO₂. In a Claus plant, the tail gas must be incinerated to oxidize the sulfur compounds to SO₂.

Absorber

After appropriate pre-treatment, the flue gas enters the SO₂ absorber, which is a simple gas-liquid contacting device with two or more absorption stages. The absorber can be designed to reduce SO₂ concentration to the required level, and can accommodate a wide range of turndown conditions. If desired, separate absorbers can be connected to each SO₂ source, with all absorbers serviced by a single regeneration system. The Wellman-Lord absorption step is free of scaling problems.

Chemical Regeneration System

Sodium bisulfite solution containing the SO_2 exits from the absorber into a surge tank. It flows at a steady rate into a forced-circulation evaporator-crystallizer, which can be heated by low pressure exhaust steam. The sodium sulfite slurry produced in the evaporator is redissolved in a dissolving tank with recycled condensate from the condenser system. The resulting lean solution flows to another surge tank and is recycled to the absorber.

Solution Surge Tanks

Fluctuations in the absorber and regeneration sections are stabilized by routing the solutions from each section through surge tanks. In addition, the regeneration section can be remotely located from the absorber section. Furthermore, the regeneration section can be shut down completely for scheduled maintenance without interrupting SO_2 removal in the absorber section. Requirements for expensive spare equipment are minimized without sacrificing basic pollution control reliability.

Purge Treatment

Oxidation of sodium sulfite in the circulating solution to sodium sulfate can occur whenever oxygen is present in the flue gas.

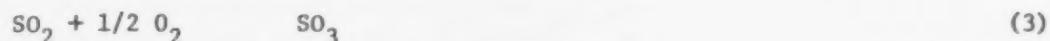
To control the level of inactive sodium sulfate in the solution, a small sidestream is sent to a purge treatment section to remove the sulfate and return active solution to the chemical section. The sodium sulfate is precipitated from the solution by cooling in a chiller-crystallizer. With controlled crystallization, the sulfate precipitates in a much greater proportion than the other sodium compounds. Thus, the solid phase is enriched in sulfate while the liquid phase becomes leaner. The solid phase is separated from the liquid, and the latter is returned to the chemical section. The solid phase can be dried for sale or for disposal. Or it can be further treated and discharged as an innocuous effluent.

Product SO_2

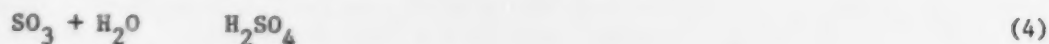
Vapor from the evaporator is cooled to condense water and achieve the desired SO_2 concentration. Wellman-Lord units treating flue gas from sulfuric acid or Claus plants recycle the SO_2 to the respective plant. The SO_2 recovered from boiler or smelter flue gases can be converted to sulfuric acid, elemental sulfur, or liquid SO_2 . A brief description for each of these processes follows:

Liquid SO_2 . The SO_2 gas is first dried with silica gel. The dry SO_2 gas is then compressed and condensed. The liquid SO_2 is collected in a pressurized storage tank.

Sulfuric Acid. The SO_2 gas and ambient air are first dried with 93% sulfuric acid. The SO_2 then reacts with oxygen, in the presence of a vanadium pentoxide catalyst, forming sulfur trioxide:

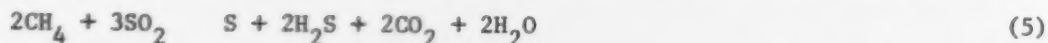


The SO_3 is absorbed from the gas mixture into 98% sulfuric acid, reacting with the dilution water to form additional acid:

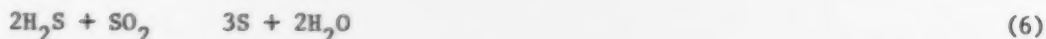


Tail gas from the acid plant is recycled to the Wellman-Lord absorber.

Elemental Sulfur. The SO_2 gas can be processed to high purity elemental sulfur. This conversion is carried out in two steps. In the first step, a portion of the SO_2 in the feed gas reacts with natural gas (methane), yielding a mixture of elemental sulfur, hydrogen sulfide, carbon dioxide and water vapor:



This reduction can also be accomplished using propane, or a reducing gas such as that from a Winkler coal gasification plant. In the second step, the H_2S reacts with the remaining SO_2 yielding additional elemental sulfur and water vapor:



The tail gas from the sulfur plant is incinerated and recycled to the Wellman-Lord absorber.

WELLMAN-LORD INSTALLATIONS TO DATE

Tables 1, 2 and 3 show Wellman-Lord installations presently operating or being designed or constructed in the U.S., Japan and West Germany.

All Wellman-Lord installations currently operating in the U.S. have an SO_2 removal efficiency greater than 90%, and an on-stream time greater than 97% for the absorption area. The installation at Standard Oil of California's (SOCAL) Richmond refinery came on stream most recently. As with its first Wellman-Lord installation at the El Segundo refinery, SOCAL waived the performance test run to determine whether SO_2 removal and other guarantees were being met. The plant's performance during the commissioning stage convinced the client of the ease of operation and the plant's ability to meet design criteria.

Additional Wellman-Lord installations at SOCAL's El Segundo and Richmond refineries are scheduled for start up this spring. Scheduled for start up at the end of March is the installation on Northern Indiana Public Service Company's (NIPSCO) Dean H. Mitchell Station Unit #11 at Gary, Indiana. This is the first application of the Wellman-Lord Process for desulfurization of flue gas from a coal fired boiler.

The largest application of the Wellman-Lord Process to date will be installed on Public Service Company of New Mexico's (PSCNM) San Juan Station Units #1 and 2 at Fruitland, New Mexico. This installation is scheduled for start-up in the summer of 1977. The Process was again selected by PSCNM for flue gas desulfurization at its San Juan Station Units #3 and 4. These installations will begin operation in November of 1978 and in April of 1980 respectively. The most recent project awarded to Davy Powergas for application of the Wellman-Lord Process is an installation for ARCO/Polymers at Monaca, Pennsylvania. Here, a single absorber will desulfurize the flue gas from three coal fired boilers with a combined generating capacity of 100 MW.

All Wellman-Lord installations currently operating in Japan also have an SO₂ removal efficiency greater than 90%, and an on-stream time greater than 98% for the absorption area.

The Wellman-Lord installations on coal fired power plants in West Germany have special significance. At both of these installations, only a portion of the boiler flue gas will be treated in the desulfurization facilities. The remainder will be mixed with desulfurized, saturated gas from the Wellman-Lord absorbers. This will provide the reheat required to prevent a steam plume when flue gas is discharged to the atmosphere. The amount of SO₂ contained in the combined stack gasses will still be less than the amount allowed by governmental SO₂ emission regulations.

These applications required a flue gas desulfurization process with a commercially proven record for high SO₂ removal efficiency and operational reliability. The Wellman-Lord SO₂ Recovery Process was selected. A U.S. utility is presently considering a proposal presented by Davy Powergas for such an installation.

UPDATED WELLMAN-LORD PROCESS FGD COSTS

Tables 4, 5 and 6 show installed capital and annual operating costs of a Wellman-Lord installation. The costs are based on a 670 MW power plant operating 8,000 hr/yr burning coal with a heating value of 8,100 Btu/lb and a sulfur content of 1.3%. The end product is sulfuric acid, elemental sulfur, or liquid SO₂. The costs are expressed in January 1976 dollars.

The capital costs presented in Tables 4 and 5 are realistic. They reflect actual Davy Powergas experience in projects which are presently in the design and/or construction phase. The capital cost presented in Table 6 includes an estimate for the liquid SO₂ plant. Therefore, it may not be as accurate as that in Tables 4 and 5. It must be pointed out that these costs are for an installation with specific parameters, i.e., power plant generating capacity, sulfur content of the coal, etc. Each of these parameters will exert a separate and distinct influence on capital cost. Therefore, each installation must be considered separately.

The consumption of utilities presented in the tables is for an installation with specific parameters. Each of these parameters will exert a separate and distinct influence on consumption of utilities. Geographical location may also affect consumption of utilities. Furthermore, unit costs of utilities will vary considerably with geographic location and with type of industry. Unit costs used in the tables are believed to be conservative.

The raw material consumed and product produced again are dependent on specific parameters of the installation. Prices for the raw material and products were obtained from a January 1976 issue of the Chemical Marketing Reporter.

The annual maintenance cost is expressed as a percent of installed capital cost per year. It reflects actual Davy Powergas experience with this type of plant. The overhead, miscellaneous, and capital recovery costs will vary from industry to industry, and even within the same industry. This is due to individual regulations or an individual company's operating and accounting philosophies. Variations in the capital recovery factor used can easily add (or subtract) several million dollars to the annual cost.

Some of the flue gas characteristics which will influence installed capital and annual operating costs are briefly discussed below.

Flue Gas Quantity

Of all the design parameters, the quantity of flue gas treated has the largest effect on the capital cost. For this reason, Davy Powergas does not require spare flue gas handling equipment. The omission of spare equipment is supported by the trouble-free operation of Wellman-Lord absorbers.

Flue Gas SO₂ Concentration

The SO₂ inlet concentration has some effect on capital cost, and a marked effect on the annual cost of utilities. As the SO₂ inlet concentration increases, the number of required mass transfer stages may decrease. This is due to the higher driving force of the more concentrated gas. For example, for 90% removal, an inlet SO₂ concentration of 1,000 PPMV may require as many as five mass transfer stages. For the same 90% removal, an inlet SO₂ concentration of 3,000 PPMV may only require three mass transfer stages. Each mass transfer stage will add two to five feet to the absorber height, and approximately three inches of water pressure drop.

Furthermore, for a given amount of SO₂ to be recovered, as the inlet concentration in the flue gas decreases, the required amount of heating steam and cooling water increases.

Flue Gas Oxygen Concentration

The formation of inactive sodium sulfate in the absorber solution varies with the oxygen concentration in the flue gas. As the concentration of oxygen increases, the size of the purge treatment section and the chemical make-up requirement will increase.

Flue Gas Particulate Loading

A wet scrubber is used upstream of the Wellman-Lord absorber to saturate the flue gas and remove its particulate content. In general, as the flue gas particulate content increases, the energy (pressure drop) required to remove particulate in the scrubber increases. The higher pressure drop will increase the booster fan power consumption. Davy Powergas recommends an efficient, dry particulate removal device upstream of the Wellman-Lord system. This will obviate the need for excessive pressure drop across the wet scrubber.

PROBLEMS FACING THE WELLMAN-LORD PROCESS AND ACTION BEING TAKEN TO RESOLVE THEM

Sulfate Purge

Oxidation of a small amount of the solution in the Wellman-Lord absorber creates the need to purge a portion of the solution from the system. This purge has two effects: a chemical make-up requirement and a potential waste disposal problem.

As the size (SCFM treated) of Wellman-Lord installations increased, the purge stream also increased. An intensive testing program was initiated to prevent solution oxidation by the addition of different antioxidants. This approach proved unsuccessful and was eventually abandoned.

Efforts were then directed toward minimizing the purge stream and the chemical make-up requirements. This was accomplished by a system that selectively removes the oxidized part of the solution by crystallization. This system achieved a five to six-fold decrease in the purge stream and the chemical make-up requirements. It is in operation at eight Wellman-Lord installations, and has been highly successful in each case.

The concentrated purge stream from this system can be dried for sale or for disposal. Or it can be further treated and discharged as an innocuous effluent. The final purge stream at NIPSCO will be dried for sale. Potential markets exist for this material throughout the U.S. In some cases, marketing the product may not be feasible.

Davy Powergas is engaged in the development of two processes to chemically reduce sodium sulfate. The purge stream would thus be regenerated and returned to the Wellman-Lord Process. One of these processes uses natural gas in the reduction step, while the other one uses coal. Both have been successfully tested on a pilot plant scale. While both processes must be optimized, Davy Powergas believes that either can be included in future Wellman-Lord installations. The Process will then produce only sulfuric acid, elemental sulfur or liquid SO_2 as a product. The chemical make-up requirement would be reduced to a minimum.

Capital and Operating Costs

All SO_2 recovery processes suffer from high installed capital and/or annual operating costs. Davy Powergas has always specified high quality proven equipment and conservatively chosen materials of construction. Undoubtedly, this is a major reason for the high reliability of the systems installed. Despite this, the Wellman-Lord Process is competitive in price with other processes.

Davy Powergas has an active program to examine ways of reducing capital and operating costs without sacrificing reliability. Several examples can be noted.

Partial Flue Gas Treatment. As previously mentioned, this concept will be applied at two West German installations and is also being considered by a U.S. utility. A potential cost reduction by use of this concept is envisioned. Based on the average of Davy Powergas projects to date, the flue gas handling area represents approximately 40% of the capital cost. Power consumption by the booster fan(s) represents approximately 70% of the annual power cost.

Sulfate Purge Concentration/Elimination. Efforts in the area of purge elimination have already been discussed. In addition, Davy Powergas is also studying a new method for sodium sulfate concentration. This method employs high temperature separation of the sulfate and has been successfully tested on a bench scale. One of the Wellman-Lord installations currently operating in the U.S. is considering installation of a pilot plant for demonstration of the method. High temperature separation of the sulfate would reduce annual cost of utilities.

Multiple Flue Gas Handling Modules. The current maximum size booster fan, scrubber, absorber module which Davy Powergas recommends will handle approximately 300,000 SCFM of flue gas. For large installations such as PSCNM's Units #1 and 2, multiple modules are required. A highly innovative concept was introduced to this application. It consists of rectangular absorbers placed immediately adjacent to each other with a common wall shared by every two absorbers. The walls will be constructed of tile lined concrete. The tile is resistant to corrosion from the circulating solution. It also provides structural support for the concrete during pouring.

SUMMARY

To summarize the preceding discussion, it is appropriate to highlight the strengths of the Wellman-Lord SO₂ Recovery Process.

Desulfurization Efficiency

From any typical fossil fuel fired boiler, an SO₂ removal greater than 90% can be achieved. Commercial units in operation consistently operate with this efficiency.

Reliability

Full scale units have demonstrated availability approaching 100% over several years of operation.

Commercially Proven

Seventeen Wellman-Lord installations in commercial service have logged an aggregate total of more than thirty-seven years of successful operation.

Saleable Product

The product from a Wellman-Lord installation is sulfuric acid or elemental sulfur. Both products are in high demand world-wide.

FIGURE 1
WELLMAN-LORD SO₂ RECOVERY PROCESS

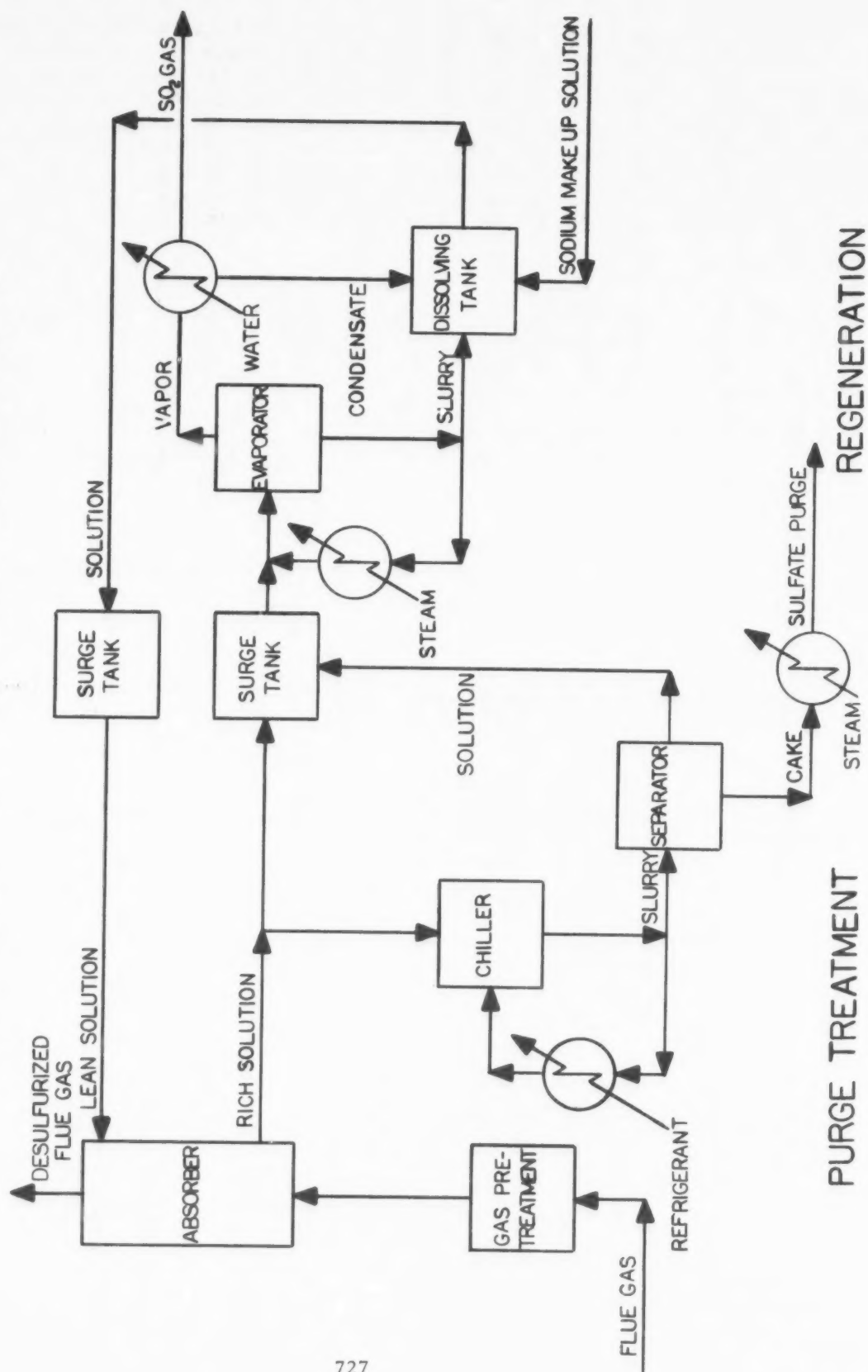


TABLE 1

WELLMAN-LORD INSTALLATIONS IN THE UNITED STATES

<u>Company and Location</u>	<u>Feed Gas Origin</u>	<u>SCFM Treated</u>	<u>Disposition of SO₂</u>
<u>Units on Stream</u>			
Olin Corp./Paulsboro, NJ	Sulfuric Acid Plant	45,000	Recycle to Acid Plant
SOCAL/El Segundo, Cal.	Claus Plant	30,000	Recycle to Claus Plant
Allied Chem./Calumet, Ill.	Sulfuric Acid Plant	30,000	Recycle to Acid Plant
Olin Corp./Curtis Bay, Md.	Sulfuric Acid Plant	78,000	Recycle to Acid Plant
SOCAL/Richmond, Cal.	Claus Plant	30,000	Recycle to Claus Plant
<u>Units in Design or Construction</u>			
SOCAL/Richmond, Cal.	Claus Plant	30,000	Recycle to Claus Plant
SOCAL/El Segundo, Cal.	Claus Plant	30,000	Recycle to Claus Plant
NIPSCO/Gary, Ind.	110 MW Coal Fired Power Plant	310,000	Elemental Sulfur Plant
PSCNM/Fruitland, N.M.	670 MW Coal Fired Power Plant	1,880,000	Elemental Sulfur Plant
PSCNM/Fruitland, N.M.	1100 MW Coal Fired Power Plant	2,510,000	Elemental Sulfur Plant
ARCO Polymers/Monaca, Pa.	100 MW Coal Fired Boiler	250,000	

TABLE 2

WELLMAN-LORD INSTALLATIONS IN JAPAN

<u>Company and Location</u>	<u>Feed Gas Origin</u>	<u>SCFM Treated</u>	<u>Disposition of SO₂</u>
<u>Units on Stream</u>			
Japan Syn. Rubber/Chiba	Oil Fired Boiler	124,000	Sulfuric Acid Plant
Toa Nenryo/Kawasaki	Claus Plant	41,000	Recycle to Claus Plant
Chubu Electric/Nagoya	220 MW Oil Fired Power Plant	390,000	Sulfuric Acid Plant
Japan Syn. Rubber/Yokkaichi	Oil Fired Boiler	280,000	Sulfuric Acid Plant
Sumitomo Chem./Sodegaura	Oil Fired Boiler	225,000	Sulfuric Acid Plant
Kashima Oil/Kashima	Claus Plant	20,000	Recycle to Claus Plant
Mitsubishi Chem./Mizushima	Oil Fired Boiler	373,000	Sulfuric Acid Plant
Toa Nenryo/Hatsushima	Claus Plant	10,000	Recycle to Claus Plant
Toyo Rayon/Nagoya	Oil Fired Boiler	218,000	Sulfuric Acid Plant
Japan Nat. Railroad/Kawasaki	200 MW Oil Fired Power Plant	435,000	Sulfuric Acid Plant
Kurashiki Rayon/Okayama	Oil Fired Boiler	248,000	Sulfuric Acid Plant
Fuji Film/Fujinomiya	Oil Fired Boiler	89,000	Liquid SO ₂
<u>Units in Design or Construction</u>			
Shin Daikyowa/Yokkaichi	Oil Fired Boiler	253,000	
Sumitomo Chem./Niigata	Oil Fired Boiler	91,000	
Mitsubishi Chem./Mizushima	Oil Fired Boiler	390,000	
Mitsubishi Chem./Kurosaki	Oil Fired Boiler	330,000	
Tohoku Electric/Niigata	100 MW Oil Fired Power Plant	236,000	

TABLE 3

WELLMAN-LORD INSTALLATIONS IN WEST GERMANY

<u>Company and Location</u>	<u>Feed Gas Origin</u>	<u>SCFM Treated</u>	<u>Disposition of SO₂</u>
<u>Units in Design or Construction</u>			
Confidential	350 MW Coal Fired Power Plant	778,000	Liquid SO ₂
Confidential	175 MW Coal Fired Power Plant	389,000	Claus Plant

TABLE 4

JANUARY 1976 COST PROJECTIONS
WELLMAN-LORD FGD PROCESS
SULFURIC ACID BYPRODUCT

Basis: 670 MW Coal Fired Power Plant
8,100 Btu/lb, 1.3% Sulfur Coal
8,000 Hr/Yr Operation

<u>Installed Capital Cost</u>	<u>\$55,500,000</u>
<u>Annual Operating Cost</u>	<u>\$ 1,000/Yr</u>
Soda Ash (\$54/Ton)	840
Steam (\$1.00/1,000 lb)	1,540
Water (\$0.03/1,000 gal)	450
Power (\$0.015/kWh)	2,680
Labor & Supervision (Labor @ \$6.00/hr)	230
Payroll & Plant Overhead (140% of Labor)	325
Maintenance (4% of Capital/yr)	2,220
Miscellaneous (3% of Capital/yr)	1,665
Capital Charges (20% of Capital/yr)	11,100
Acid Credit (\$24/Ton)	(2,830)
<u>Total</u>	<u>\$18,220</u>

Installed Capital Cost \$83/kW
Annual Operating 3.4 Mils/kWh

TABLE 5

JANUARY 1976 COST PROJECTIONS
WELLMAN-LORD FGD PROCESS
ELEMENTAL SULFUR BYPRODUCT

Basis: 670 MW Coal Fired Power Plant
8,100 Btu/lb, 1.3% Sulfur Coal
8,000 Hr/Yr Operation

<u>Installed Capital Cost</u>	<u>\$58,500,000</u>
<u>Annual Operating Cost</u>	<u>\$ 1,000/Yr</u>
Soda Ash (\$54/Ton)	840
Steam (\$1.00/1,000 lb)	1,380
Water (\$0.03/1,000 gal)	420
Power (\$0.015/kWh)	2,590
Natural Gas (\$1.50/MM Btu)	790
Labor & Supervision (Labor @ \$6.00/hr)	230
Payroll & Plant Overhead (140% of Labor)	325
Maintenance (4% of Capital/yr)	2,340
Miscellaneous (3% of Capital/yr)	1,755
Capital Charges (20% of Capital/yr)	11,700
Sulfur Credit (\$60/Ton)	(2,310)
<u>Total</u>	<u>\$20,060</u>

Installed Capital Cost \$87/kW
Annual Operating Cost 3.7 Mills/kWh

TABLE 6

JANUARY 1976 COST PROJECTIONS
WELLMAN-LORD FGD PROCESS
LIQUID SULFUR DIOXIDE BYPRODUCT

Basis: 670 MW Coal Fired Power Plant
8,100 Btu/lb, 1.3% Sulfur Coal
8,000 Hr/Yr Operation

<u>Installed Capital Cost</u>	<u>\$56,000,000</u>
<u>Annual Operating Cost</u>	<u>\$ 1,000/Yr</u>
Soda Ash (\$54/Ton)	840
Silica Gel	Nil
Steam (\$1.00/1,000 lb)	1,540
Water (\$0.03/1,000 gal)	420
Power (\$0.015/kWh)	2,710
Labor & Supervision (Labor @ \$6.00/hr)	185
Payroll & Plant Overhead (140% of Labor)	255
Maintenance (4% of Capital/yr)	2,240
Miscellaneous (3% of Capital/yr)	1,680
Capital Charges (20% of Capital/yr)	11,200
SO ₂ Credit (\$110/Ton)	(8,460)
<u>Total</u>	<u>\$12,610</u>

Installed Capital Cost \$84/kW
Annual Operating Cost 2.4 Mills/kWh

SUMMARY OF OPERATIONS OF THE CHEMICO-BASIC MgO FGD SYSTEM
AT THE PEP/CO DICKERSON GENERATING STATION

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ABSTRACT

The Chemico/Basic MgO FGD prototype regenerative wet scrubbing system at Potomac Electric Power Company's Dickerson Generating Station is reviewed. Objectives of the two-year prototype test program are stated and operational experience is summarized. Attainment of the objectives in terms of process, performance, equipment operation, and economics is evaluated. Projected costs and future direction of wet scrubbing at the Dickerson Station are also discussed.

SUMMARY OF OPERATIONS OF THE
CHEMICO-BASED MgO FGD SYSTEM
AT THE PEPCO DICKERSON
GENERATING STATION

INTRODUCTION

In September 1970, the Potomac Electric Power Company, (PEPCO) selected the Chemico-Basic MgO Process for flue gas desulfurization of one of its coal-fired boilers to demonstrate the feasibility of regenerative wet scrubbing.

The process utilized a two-stage vessel - the first stage for particulate removal, and the second stage for SO₂ absorption using MgO as the absorbing alkali. The particulate stage handles flue gas from either the inlet or the outlet of an electrostatic precipitator. The purpose of varying the particulate inlet loading was to determine how much particulate contamination can be tolerated in the SO₂ removal stage and to determine the overall effect on particulate removal by the first stage.

Pilot testing was performed at the Dickerson Station Unit No. 3 to evaluate system operating and performance conditions as well as to evaluate certain process factors in the scrubber recycle liquid system. Testing was a follow-on to the Boston Edison/Chemico-Basic/EPA MgO-SO₂ removal system on an oil fired installation at Boston Edison's Mystic Station. Some modifications made to the Dickerson Unit during its design and construction were the result of experience gained on the Boston Unit, although many of the system components remained the same because of the closely concurrent schedules of both installations.

The objectives of the project were to:

1. Achieve 90% or more SO₂ removal efficiency using MgO as the absorbing agent,
2. Determine the effect of particulates on SO₂ absorption and to evaluate the effect of inlet grain loading on particulate collection efficiency,
3. Produce anhydrous magnesium sulfite for ultimate conversion to MgO and re-use as an SO₂ absorbant,

4. Produce commercially salable sulfuric acid made from the absorbed SO_2 ,
5. Determine the impact of boiler load swings upon the scrubbing system performance as related to materials storage and handling,
6. Obtain data relating to system efficiency, energy requirements, mechanical performance, maintenance, and overhead burdens to project operating costs for 600 Mw installations or larger,
7. Optimize design parameters so that capitalization for systems of more than 600 Mw could be determined.

This paper reviews the prototype system, and examines its performance, equipment design and operation, process, and resulting economics.

SYSTEM DESCRIPTION

Figure 1 is a cutaway section of the 2-stage scrubber. The scrubber vessel consists of a variable throat venturi in the first stage for flyash removal and a fixed throat in the second stage for SO_2 absorption.

Flue gas enters the scrubber at 250°F and is saturated and cooled to 120°F in the first stage where flyash is removed. In the second stage the flue gas is contacted with atomized MgO slurry for SO_2 absorption. It then passes through a mist eliminator section within the vessel.

Figure 2 is a schematic of the Dickerson Regenerative Wet Scrubbing System. The system was designed to treat one half of the flue gas of a 190 Mw boiler, or 295,000 ACFM. It is capable of taking flue gas, both before and after an electrostatic precipitator.

After leaving the scrubber, the flue gas proceeds through the I.D. fan and a separate mist eliminator before entering the breeching of the stack.

The liquid streams are distinct and separate, one for each stage. The first stage utilizes two 100% recycle pumps of alloy 20 construction. A stream is bled from the discharge of these pumps to two 40' diameter thickeners. The overflow water from the thickeners is returned to the scrubber; thickener underflow is diluted and pumped to a pond approximately 2000 feet away.

The second stage has three 50% recycle pumps. The MgSO_3 bleed stream is taken

from the second stage recycle pump discharge and brought to a centrifuge. The magnesium sulfite cake from the centrifuge is further dewatered and dried in a cocurrent rotary dryer and stored in silos for transportation to the calcining facility. Centrate from the centrifuge is used to slake all magnesium oxide feed.

The dryer off-gas is returned to the second stage of the scrubber vessel. As originally designed, this stream of 450°F gas was to be returned to the scrubber outlet duct for reheating the flue gas. However, during initial operation of the Boston Edison Unit it was discovered that this was a source of MgO loss as the MgO would go up the stack and fall out onto the surrounding area.

The silo storage capacity is based upon six days of full load operation.

OPERATION

Initial start-up was in September 1973 and the system was operated until January 1974. Problems during this period ranged from corrosion leaks resulting from non-specified material in expansion joints, to minor mechanical problems in material handling equipment, to problems in the feeding and slaking of MgO, to plugging in the MgO mix tank and suction lines to the MgO make-up pumps.

Maintenance and modifications were performed on the system from January to April 1974. The major modification was the addition of a pre-mix tank in the MgO feed system. The system was again started in April. Operations from April to July 1974 were limited, however, as PEPCO did not have access to the EPA calcining facility located at the Essex Chemical Company sulfuric acid plant in Rumford, Rhode Island. EPA had built and operated the calcining facility as part of the demonstration of the MgO process at Boston Edison. PEPCO was to use this facility upon completion of the Boston Edison test program, but it became apparent that the calcining facility would not be available prior to July. By the end of June 1974, all the MgO at Dickerson had been used and a silo and three rail cars were full of magnesium sulfite.

Rumford started calcining the PEPCO sulfite in July 1974. It was discovered that the sulfite from the coal-fired Dickerson Station was different from the

sulfite from the oil-fired Mystic Station, necessitating some testing to determine the proper operating parameters for calciner operation. In August 1974 the Dickerson scrubber system was started and the MgO slaking problems appeared to be eliminated by the pre-mix tank. The Rumford calciner was ready and arrangements were made for trucking the material between Dickerson and Rumford. A decision was made to use a relatively low inventory of MgO in order to obtain the maximum number of regeneration cycles possible in the planned operational period scheduled to end on December 31, 1974. During this time most of the system operated at 75% of design gas flow.

A problem developed in the bucket elevator carrying magnesium sulfite from the dryer to the storage silo. At design load, the buckets, when slugged with material, tended to overload and trip. The slugging was traced back to the discharge chute from the centrifuge. Material hung up in the chute fell into the screw conveyor, thereby slugging the dryer. The dryer held material a little longer before slugging the bucket elevator, and this limited continuous operation at design gas flow.

Unit No. 3 was taken out of service in February 1975 for an 8 to 12 week turbine overhaul. At this point, most of the technical data required for confirming the process had been obtained. During this period the scrubber system was inspected and maintenance and modifications made. Unit No. 3 remained shut down until July 1975. Modifications made during this period were the design of the centrifuge outlet hopper to improve flow, and the installation of larger buckets on the sulfite elevator.

System maintenance included minor repairs to the flake glass lining in the vessel, replacement of several sections of first-stage rubber-lined pipe, and replacement of sections of the second stage carbon steel pipe. All of this work was based on the minimum necessary to place the system in condition for a three (3) month run.

The FGD system was re-started in August 1975. Although start-up was smooth, steam was lost to the MgO mix tank resulting in a very wet product from the centrifuge. Operation continued, but caking in the dryer occurred. This was believed to be caused by unreacted MgO carryover due to lack of heat in the MgO

mix tank. The dryer was then cleaned and the steam line repaired. The system was re-started and again a wet product and caking in the dryer was experienced. The system was shut down in order to determine the cause and corrective actions to be taken. It was decided to make some adjustments to the centrifuge to see if it would extract more water. During this period, PEPCO decided to test only the first-stage, taking gas ahead of the precipitator. When this testing was completed an attempt was made to start the second stage but the centrifuge had frozen, probably due to inadequate flushing on shutdown.

FGD operation at Dickerson terminated at this point.

Operation in the particulate removal mode continued. The objective was to obtain information on sustained operation for 10 to 20 days. It was previously reported that problems existed with rubber-lined pipe. This piping was replaced, and during this run, which was terminated by choice after 20 days, no failures in rubber-lined pipe occurred.

RESULTS

Results of performance, hardware, process, and economics for two years of operation are summarized below:

Performance

Test data show that first stage particulate removal is very efficient. The outlet particulate loading from the scrubber is continually below .02 grains/SCF dry whether the scrubber is accepting flue gas from ahead of or after the electrostatic precipitator, and at any flue gas volume up to design flow. Inlet loading to the scrubber ranged from .06 g/SCF dry to 4.5 g/SCF dry. The SO₂ removal system was designed for 90% removal efficiency when burning 3% sulfur coal, which equates to 1850 PPM inlet SO₂ loading. Although actual operation above 1700 PPM inlet did not occur, there is no doubt that the system is capable of meeting design. The SO₂ removal efficiency was consistently above 90% whenever operating at design gas flow and inlet concentrations above 1000 PPM.

Hardware

Generally, the major items of equipment operated well throughout. The scrubber vessel, fan, thickeners, centrifuge, and dryer all performed well.

A great deal was learned about the materials required for handling MgO slurry. The carbon steel pipe and slurry feed pumps for this service were not adequate for the corrosive-erosive action of the slurry. Individual feed pump suction and discharge lines were found to be very desirable. The material handling system was an area which required improvement in items such as the bucket elevator, the centrifuge discharge hopper, and the weigh belt feeders.

In addition to obtaining test data, every effort was made to achieve maximum operating hours. The major cause of forced outages during this period were failures in the first and second stage piping. The first stage piping is rubber-lined and it was difficult after a failure of the lining to determine the cause. In some cases, the lining has appeared thinner than specified and not properly bonded to the pipe. However, there have been no failures in any rubber-lined piping since replacement. The second stage piping is carbon steel and the problem was a combination of corrosion-erosion.

The materials of construction in the first stage were specified for low pH and abrasive material service. The MgO stage was essentially carbon steel and did not allow for the abrasiveness of MgO nor did it provide for excursions into the very low pH range when difficulty was experienced in slaking and adding MgO. Inspection of the scrubber vessel, however, revealed it to be in good condition. There was no scaling or build-up problems. There were some spots in the vessel where the protective polyester flakeglass lining was worn. These were, for the most part, random small spots. In the second stage throat there was erosion of the lining caused by a modification that was made to increase pressure drop. This modification distorted the venturi flow. Some failure spots of the lining were caused by pieces of tramp material damaging the lining. The wet I.D. fan was very clean.

Following are some of the unknowns that may have had an effect on the wet centrifuge product:

1. Internal problem with the centrifuge due to wear or buildup of material.
2. Change in the MgO. This was the first time that a mixture of re-generated MgO from the Boston-Edison and PEPCO projects was used.

3. Appearance of the centrifuge cake was similar to that of the tri-hydrate but analyses showed it was still the hexa-hydrate.

It should be noted that the dryer is designed with internal chains to allow for operation with a wet product. These chains were never installed in the Dickerson dryer. With chains in the dryer, continued operation with the wet product should be possible.

Process

The process has demonstrated that it can achieve a 90% or better SO_2 removal efficiency. It can produce commercially salable sulphuric acid, and MgO can be recycled and used in the absorber.

Process related problems appeared in two areas:

1. MgO slaking and injection were clearly the most troublesome areas. It is now known that regenerated MgO and the virgin MgO have widely varying physical properties. The virgin material is very dusty and presents buildup problems in the feed chute. It also resists wetting and agglomerates in large chunks which would block pump suction lines. The addition of a pre-mix tank and high speed agitator solved this problem. The regenerated MgO had different physical properties, practically no dusting problem, and requires an elevated temperature to maintain its SO_2 absorption capacity.
2. The MgSO_3 product obtained in the pilot plant had a hexa-hydrate crystal. At Boston Edison, the tri-hydrate crystal was predominant in the MgSO_3 and initially caused material handling problems. Although the Dickerson Unit produced a product which was approximately 90% hexa-hydrate MgSO_3 , there were times when this percentage diminished in favor of the tri-hydrate form, and may have contributed to the material handling problems.

Economics

As mentioned earlier, one purpose of the demonstration project was to develop cost estimates to project the economic impact of a full-scale system applied to

a unit or total plant. The actual costs incurred during the operation of the Dickerson units are not too meaningful when quoted in absolute dollars, but the technical knowledge learned can be input into the second generation design and gives a utility a yardstick to use in evaluating a proposed design.

To give an idea of the costs of operating the prototype scrubber, PEPCO, in 1974, spent \$493,000 in operation and maintenance, and \$435,000 in operation and maintenance of the Rumford facility, including trucking material to and from the site. In addition, Chemico contributed six months of project management and three shift advisors at Dickerson, and EPA retained York Research to do test work.

For forecasting the economics associated with the MgO process, the existing Dickerson Station will be used. The Dickerson Station consists of three units each rated at 190 Mw (gross). The planned Unit 4 addition, rated at 850 Mw (gross), is located about one-half mile from the existing plant and is scheduled for operation in the Spring of 1982.

Following are the assumptions pertaining to the design of a MgO desulfurization system. No decision has been made to install a desulfurization system; this is for evaluation purposes only.

1. Flue gas from the three existing units will be headered, passed through a two-stage scrubber system for particulate removal and SO₂ absorption, and the scrubbed flue gas discharged to a single new tall stack.
2. The new Unit 4 will be equipped with high performance hot electrostatic precipitators with a guaranteed outlet dust loading of less than .02 grains/SCFD. Space also will be left for the future addition of particulate scrubbers.
3. The proposed design includes a common facility for MgO storage, MgSO₃ storage, and an on-site sulfuric acid plant. This facility is located midway between the old and new plants.
4. The assumption is made that the sale of sulfuric acid will cover the

fixed charges, the operation, and the maintenance costs associated with the acid plant.

5. Capital costs of scrubbing systems for the three existing units, the one new unit, and common facilities (excluding the acid plant), are difficult to determine. The estimated costs in 1975 dollars is in the range of \$130,000,000 to \$150,000,000 including the cost of a new 700 foot stack. Based on escalation of 9% per year, Units 1, 2, and 3 in-service January 1980, and Unit 4 in-service January 1982, the cost escalated to the \$170,000,000 to \$200,000,000 range. A problem in determining the costs of a new unit is to decide what should be included as part of the scrubber system. For instance: Should any part of the precipitator be charged to the scrubber, how much of the fan cost, duct work, foundation, land, etc. be charged?
6. Engineering for four units is done concurrently. Part of Unit 4 common facilities such as foundations will be done with Units 1, 2, and 3.
7. All four units will be assumed to operate at a 75% capacity factor producing a net output of 8.8×10^9 KWHS per year.

The problem is to translate these assumptions into the cost of producing electricity. Based on PEPCO's evaluation of the scrubber system, operation of Units 1, 2, and 3 will require a minimum of two operators per shift plus proportionate time of the shift supervisor. The Unit 4 scrubbers which are located one-half mile from the existing units will also require two operators per shift and supervision. The common facility will require an estimated three men per shift. Maintenance for the total complex will need an additional four men per day. Total complement for stack gas desulfurization is, therefore, estimated at a minimum of 39 men.

It is estimated that the system would burn in excess of 30 million gallons of No. 2 fuel oil per year at Dickerson, but No. 6 could be used for the dryer, calciner, and reheater at some other site. About 2% - 3% of the station's output will be required for station service. MgO makeup is estimated at 7%. Figure 3 is a tabulation of the estimated annual expenses.

SUMMARY

PEPCO operates three base loaded generating stations in Maryland - the Dickerson Units, 570 Mw; Chalk Point - 1300 Mw; and Morgantown - 1148 Mw. It should be noted that all three of these stations meet EPA primary air quality standards for ground level SO₂ concentrations when burning coal containing approximately two(2)% sulfur. A 630 Mw addition is planned for Chalk Point in 1980, and an 850 Mw addition at Dickerson in 1982. To install stack gas desulfurization systems at all three of the above plants for the total planned capacities will require a capital investment of close to \$500,000,000. In addition, it will be necessary to install an additional 133 Mw of capacity to replace the loss of capacity due to scrubbers. This would require an additional 30 to 80 million dollars, depending on the type of capacity (base or peaking) installed.

Testing has shown that taking half the flue gas from ahead of the existing electrostatic precipitator, passing it through a particulate scrubber and mixing it with the other half of the flue gas for reheat, will result in compliance with particulate emission regulations for the Dickerson Station. PEPCO is proceeding to modify the Chemico scrubber system to have it operational on a full-time basis by the end of 1976 as a particulate scrubber. Scrubbers will be added to Units 1 and 2 for particulate scrubbing only. These will be two-stage vessels to allow for the future addition of an SO₂ removal loop, if required. It should be noted that the current operation of the Dickerson Station, burning up to two(2)% sulfur coal, is in compliance with EPA primary air quality standards for ground level SO₂ concentrations.

PEPCO believes that regulatory agencies should work closely together to achieve the goal of reliable power with an improved environment for the customer and at the lowest cost to the customer. PEPCO feels that each power plant should be assessed on its particular environmental impact, and controls should be required based only on this impact. For instance, at Dickerson, when its capacity is expanded by the addition of a new 800 Mw unit now scheduled for 1982, it is quite possible that ground level SO₂ concentrations can be met by scrubbing only a portion of the flue gas. PEPCO believes this would result in substantial capital savings, lower operating costs, and, most important at Dickerson, considerable savings in No. 2 fuel oil due to stack reheat being obtained from the mixture of scrubbed and unscrubbed flue gases in the stack.

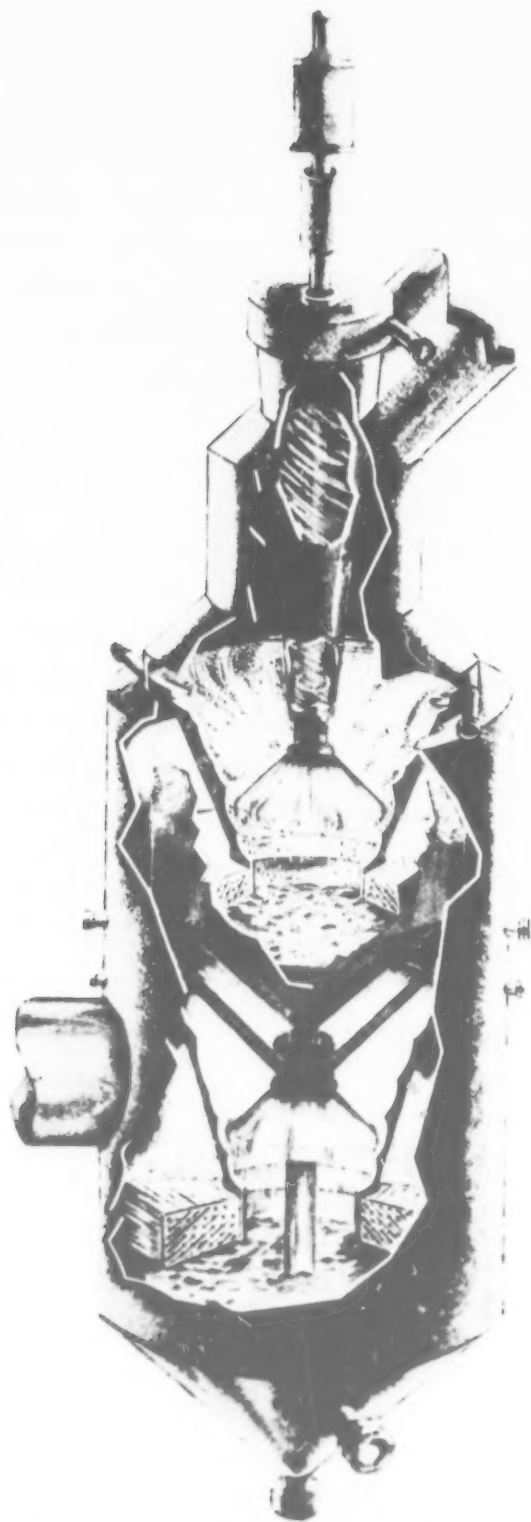


Figure 1. Two - stage venturi scrubber.

<u>ANNUAL COSTS (1975 \$)</u>	<u>\$ x 10⁻⁶</u>	<u>MILLS/KWHR</u>
Fixed (15%)	21.00	2.39
Operating Labor	.60	.07
Operating Supplies	1.00	.11
MgO (7% Make-Up)	1.20	.14
Maintenance	3.00	.34
No. 2 Fuel Oil @ 30¢/gal.	9.00	1.02
Contingency (10%)	1.48	.17
Electricity	<u>3.75</u>	<u>.43</u>
Sub-Total	41.03	4.67
Fixed Charge on Replacement Capacity	<u>3.78</u>	<u>.43</u>
TOTAL	<u>44.81</u>	<u>5.10</u>

Figure 3. Tabulation of Estimated Annual Expenses.

MAGNESIUM OXIDE SCRUBBING AT
PHILADELPHIA ELECTRIC'S EDDYSTONE STATION

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ABSTRACT

The particulate and sulfur dioxide removal system at Philadelphia Electric's Eddystone Station employs a two-phase approach to air pollution abatement. Phase I consists of complete particulate scrubbing on Eddystone Unit 1 (314 MW net) and one-third sulfur dioxide scrubbing to develop an optimized system for Phase II, which will consist of complete particulate and sulfur dioxide removal systems on Eddystone Units 1 and 2.

The Phase I sulfur dioxide removal system uses magnesium oxide in a recovery system to ultimately produce sulfuric acid. An off-site MgO regeneration facility is included to close the scrubbing loop.

The system start-up and initial operation have uncovered some problems to be described in this presentation together with some project delays.

MAGNESIUM OXIDE SCRUBBING AT PHILADELPHIA ELECTRIC'S EDDYSTONE STATION

Philadelphia Electric Company embarked on a program to install a particulate and sulfur dioxide scrubber system at Eddystone Station in mid-1971. This paper reviews briefly the system design, highlights the problem and working areas on particulate scrubbing, the problem areas on sulfur dioxide scrubbing and reviews the projected schedule for the continuation of this developmental system.

SYSTEM DESIGN

The scrubber plant at Eddystone Unit 1 consists of three parallel scrubbing trains with a particulate scrubber, reheater and scrubber booster fan in each train. One train also has the SO_2 scrubber in series with the particulate scrubber (Figure 1). Flexibility for operation was incorporated in the ductwork through systems that permit bypassing the SO_2 scrubber, each train or the entire scrubber plant, since this system was retro-fitted between the Unit induced draft fans and stack.

The particulate and SO_2 scrubbers have separate surge tanks for slurry collection, pH control and make-up (Figure 2). These surge tanks were carbon steel with a polyurethane coating, and the SO_2 scrubber is also carbon steel with the same coating. The particulate scrubbers are 316 L stainless steel and the piping systems are all rubber-lined.

MgSO_3 blowdown from the SO_2 scrubber is recovered by dewatering in a series combination thickener - centrifuge, drying in a rotary-kiln drier and storage in a silo for shipment to the off-site MgO regeneration facility (Figure 3).

The SO_2 scrubber incorporates two (2) stages of scrubbing venturis and two stages of mist elimination (Figure 4).

Dry powder MgSO_3 is calcined in a fluid bed reactor in the off-site MgO regeneration facility (Figure 5). This facility includes an air preheater, cyclone separator system, venturi scrubber and gas cooling tower for the separation of the MgO crystals, and the cleaning and cooling of the SO_2 rich gas for transfer to the sulfuric acid plant. This facility is located at the OLIN Corporation sulfuric acid plant in Paulsboro, NJ, across the Delaware River from Eddystone. The transfer of dry material, MgO and MgSO_3 , between Eddystone and Paulsboro is by truck transportation.

OPERATING PERIODS

There was a brief operating period on the particulate scrubbers from mid-November, 1974 into March, 1975, that uncovered a number of problem areas, which are outlined later in this paper. Due to a number of extenuating circumstances the scrubbing was not restarted until July 23, 1975 with one particulate scrubbing train, 1-C, followed by the other two trains, 1-B and 1-A, on August 15 and October 2, respectively. The SO₂ scrubber, 1-C, was started for the first time also on October 2, 1975, and the MgO regeneration facility first processed MgSO₃ from the Eddystone scrubber on October 28, 1975.

The 1-C particulate scrubber train has had the most operation with a total of 2831 hours through January 31, 1976, with an availability of 70% since July 23, 1975. Priority for operation was given to this train, since the one (1) SO₂ scrubber is in series with it, when operated.

The 1-B particulate scrubber train has been operated for a total of 1933 hours through January 31, 1976, with an availability of 53% since August 15, 1975.

The 1-A particulate scrubber train has been operated for a total of 626 hours through January 31, 1976, with an availability of 24% since October 2, 1975.

The 1-C SO₂ scrubber loop has been operated for a total of 556 hours through December 31, 1975, with an availability of 33% since October 2, 1975.

The MgO regeneration facility has been operated to process all MgSO₃ material sent to it from Eddystone. This operation was usually on a batch basis due to the ups and downs at the Eddystone scrubber.

PROBLEM AREAS - PARTICULATE SCRUBBING

The problems referred to previously in the brief operation period of November, 1974 to March, 1975, centered around the scrubber booster fans and the flue gas and liquid conditions.

The 1-B scrubber booster fan, when started for the first time, developed high shaft vibration after about 1 to 1½ hours. Since all three (3) fans are identical, it was imperative to determine and correct the problem. The problem was that this fan had an excess clearance of the slip fit between the shaft and the wheel hub that caused high vibration upon reaching operating temperature. Fortunately, this fan was not on the train that has the SO₂ scrubber, and, while it was returned to the factory for a shrink fit repair, we concentrated on operating the 1-C train with the SO₂ scrubber.

The next problem during this early operating period was corrosion of the 1-C particulate scrubber internals. This scrubber is made of 316 L stainless steel with a 2.75% min. molybdenum content. During a 100 hour run we had experienced a slurry pH level as low as 0.5, and a chlorides level of 2000 + ppm. These conditions, coupled with the thermal shock of our "hot start" procedure, caused this corrosion, because, with caustic addition for pH control at 2.5, higher blowdown to reduce the chlorides level and a "cold start" procedure the corrosion has been reduced materially.

About this time we had been checking out the 1-C SO₂ Scrubber with water to check out flow rates and spray patterns. As mentioned before, this scrubber and its surge tank were carbon steel with a polyurethane coating, and, after this check-out, we found the coating of these two vessels was blistering and peeling. An immediate inspection of the particulate surge tanks revealed a similar problem, although not as extensive. However, the particulate scrubber surge tanks now operated at 2.5 pH, while the SO₂ scrubber surge tank would operate at 6.5 pH. Thus, we proceeded to blast and recoat the three (3) particulate surge tanks with a "flake glass" polyester coating. This recoat was delayed by an operating engineers strike, which forced our re-start into July, 1975.

The other problem areas to be highlighted here have occurred during our more continuous operation from July 23, 1975 to January 31, 1976.

Circulating Pump Capacity

The circulation pumps for spray supply on the particulate scrubbers are direct-drive, open impeller, rubber-lined impeller and casing with a capacity of 1500 gpm. However, the capacity checks indicated only 1200 gpm at rated motor current, which did not adversely affect the 1-B and 1-C particulate scrubbers. The other, 1-A, due to its design, needs full 1500 gpm flow to insure good mixing and fully wetted walls. This problem is being resolved with the pump manufacturer.

By-Pass Damper Drive Units

One critical point in the by-pass system are the three (3) scrubbing plant by-pass dampers located between the supply and return headers. These dampers permit complete, partial or zero flue gas flow around the scrubbing plant and were designed for two (2) second opening to prevent upsetting the main unit on a scrubber train malfunction. The drive unit on these dampers is a pneumatic cylinder operating through a lever arm to obtain 90° rotation in this short time. The lever arm attachment to the damper shaft end has failed a number of times following a "scram" or snap-action. Heavier design lever arms with longer stroke pneumatic cylinders are being installed at this time, while the main unit is shut-down for an eight (8) week overhaul.

Reheat Burner Refractory Failure

The three (3) reheat burners consist of an oil torch mounted in a separate combustion chamber at right angles to the flue gas duct upstream of the scrubber booster fans. The combustion chamber is five (5) foot in diameter, eight (8) feet long and double-brick refractory-lined. This refractory has failed due to the criticality of torch placement and start-up problems with the ultra-violet flame scanners. In addition, insulation had been placed on a small section of the chamber, which did not allow heat dissipation and subsequent failure of the refractory and steel shell. We are still working on this failure.

WORKING AREAS - PARTICULATE

There are a number of areas in the particulate scrubbing plant that have been working well and are worthy of notice here.

Scrubber Train Isolation Valves

Each train has an inlet and outlet flue gas valve (damper) for the purpose of isolating the train while on by-pass operation. These valves were specified for practically zero leakage in order to do maintenance on the scrubbers, reheaters, duct instrumentation and booster fans. These valves are a single 130 inch disk that is lever-guided as opposed to a center shaft butterfly. The lever-guiding mechanism permits a single surface seat and disk for sealing, and they have performed very well. We have had no problems in working on the equipment, while the main unit was in service.

Particulate Scrubber Performance

Scrubber performance tests were just completed before the present outage on the main unit, and test results are expected within the next week. However, preliminary indications are that the ash quantity going into these scrubbers is about seven (7) times greater than design due to poorer coal conditions and deterioration of the mechanical collectors and electrostatic precipitators on the main unit. The stack appearance, when all three (3) scrubbers are in service, would say they are doing quite a job on this quantity of ash.

Mist Eliminator Performance

Performance testing in this area was also just completed and the test results are also awaited.

Surge Tank Recoating

The "flake-glass" polyester recoating on the three (3) tanks is holding up very well so far.

PROBLEM AREAS - SO₂ SCRUBBING

The short time that the SO₂ scrubber loop has been in service has uncovered some mechanical problems and some chemical problems. Due to the short operating time, only those problems that we have a good handle on will be reported.

Circulating Pump Motor Base

The three (3) circulating pumps on the SO₂ scrubber are belt-driven, open impeller, rubber-lined impeller and casing rated at 6500 gpm. The belts are of the "poly-V" design and tensioning is with a slide mechanism under the motor base. This slide mechanism is too light-duty for this service and has failed. A redesign is being incorporated.

MgSO₃ Carryover

The SO₂ scrubber has two stages of venturis and two stages of mist eliminators. With both stages of scrubbing in service there is an excess carryover of slurry from the second stage into the first mist eliminator catch troughs, causing the overflowing of the mist eliminator tank. A series of deflectors will be installed to prevent this excess carryover.

MgO Slaking

The MgO powder is slaked in the slaking tank equipped with an agitator and heating coils. The MgO was first slaked with the liquor removed by the centrifuge, but this caused the formation of grits that plugged the lines and transfer pumps. A pre-slaker arrangement will be tried when the scrubber returns to service.

PROJECTED SCHEDULE

All of the problem areas reported have contributed to the extension of our schedule. In addition we have recently had to change the direction of our SO₂ removal system "closed loop" due to the shutdown of the OLIN sulfuric acid plant on December 31, 1975. This means we must relocate our MgO regeneration facility in order to continue developing the system for additional installations on the P.E.Co. system.

This relocation of the facility is still being worked out, but it will probably extend our developmental schedule by almost one (1) year to mid-1977.

The particulate and sulfur dioxide removal system described here on Eddystone Unit 1 is the first phase of a two-phase project. Following the successful line-out of this system with more continuous operation, it will be incorporated into the design for the complete sulfur dioxide removal on Eddystone Unit 1, and particulate and sulfur dioxide removal on Eddystone Unit 2 and one of two units at our Cromby Station.

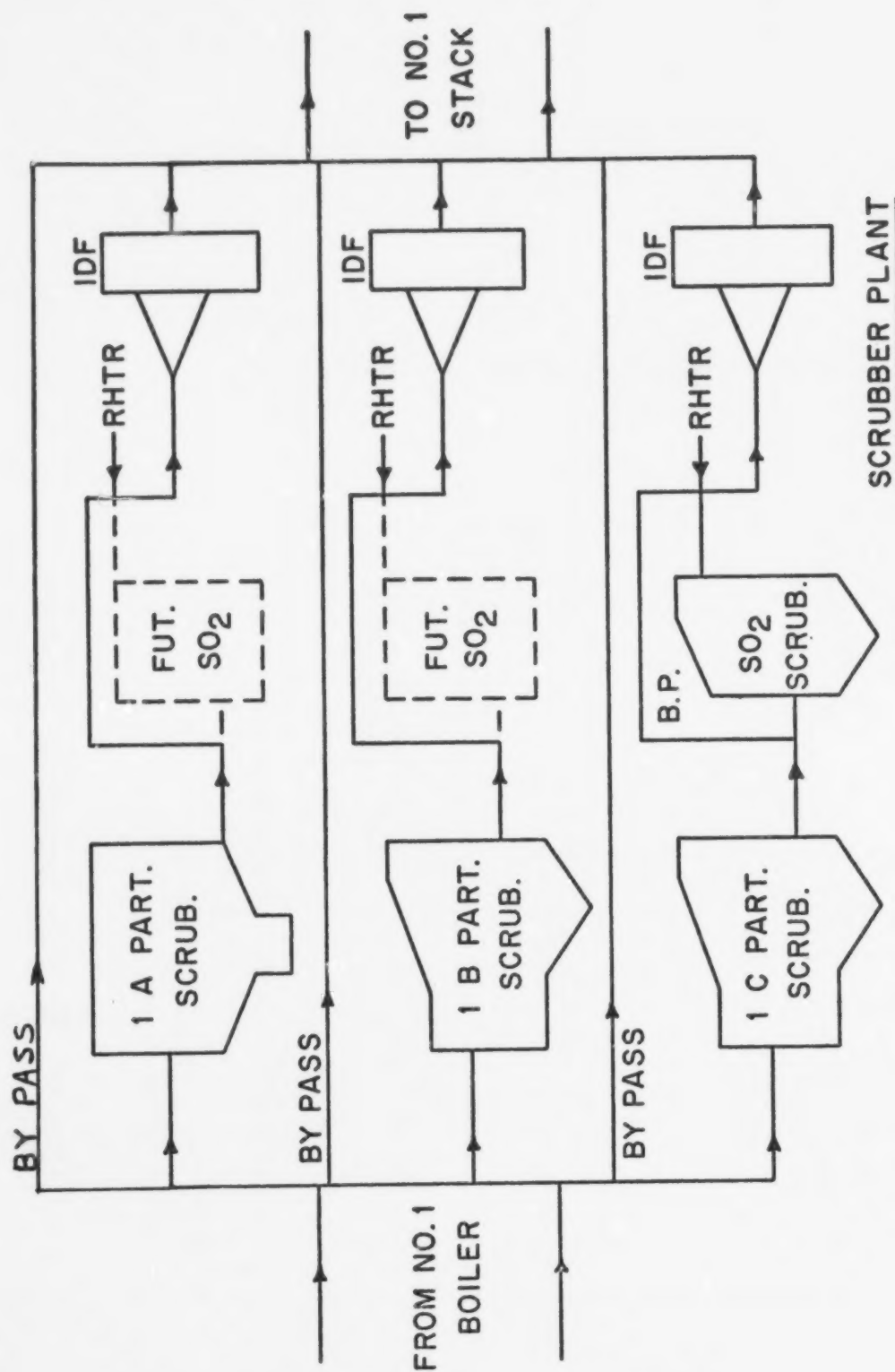


Figure 1. Eddystone no.1 SO₂ removal - phase 1.

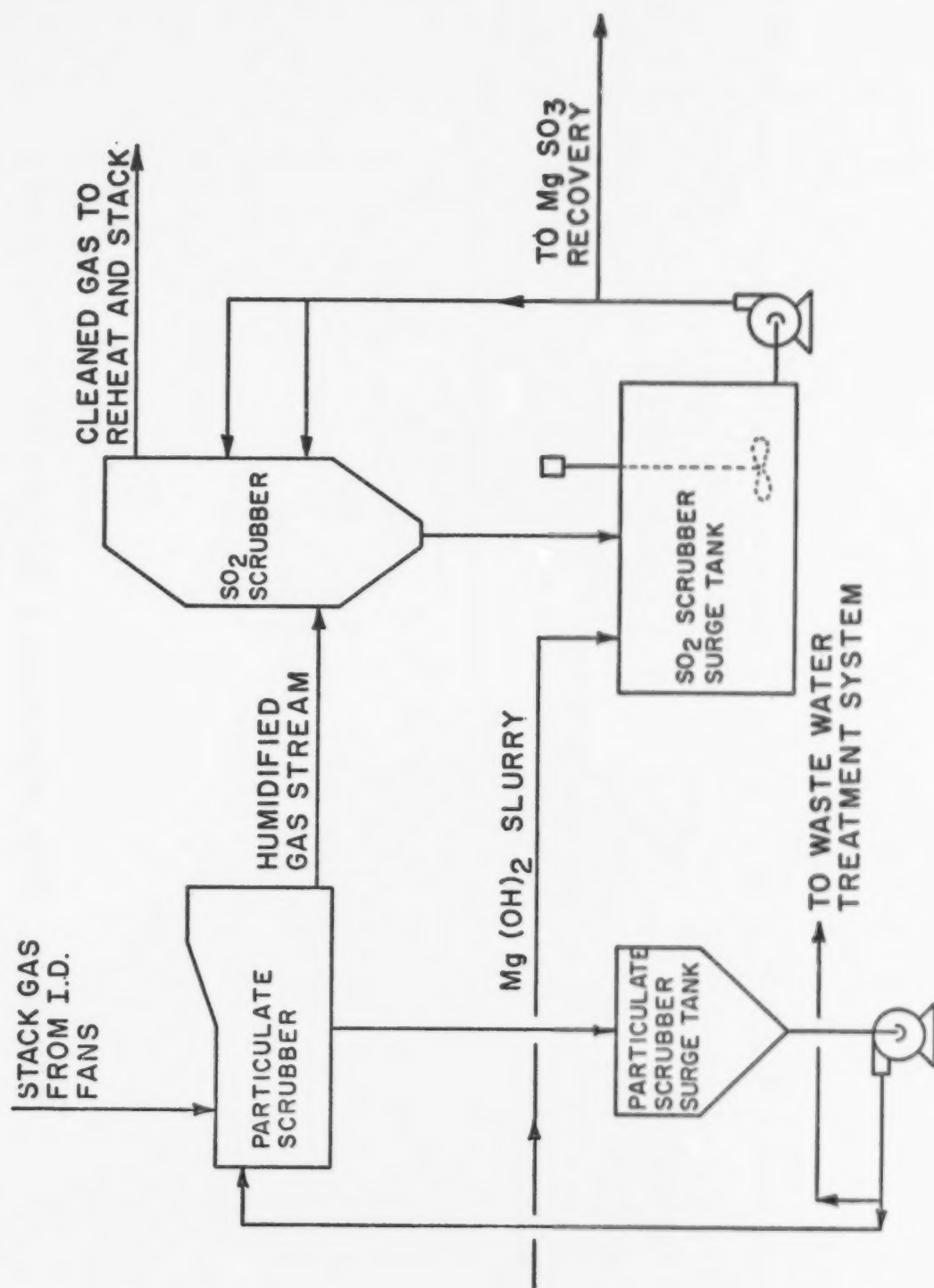


Figure 2. SO₂ scrubber system - SO₂ scrubber.

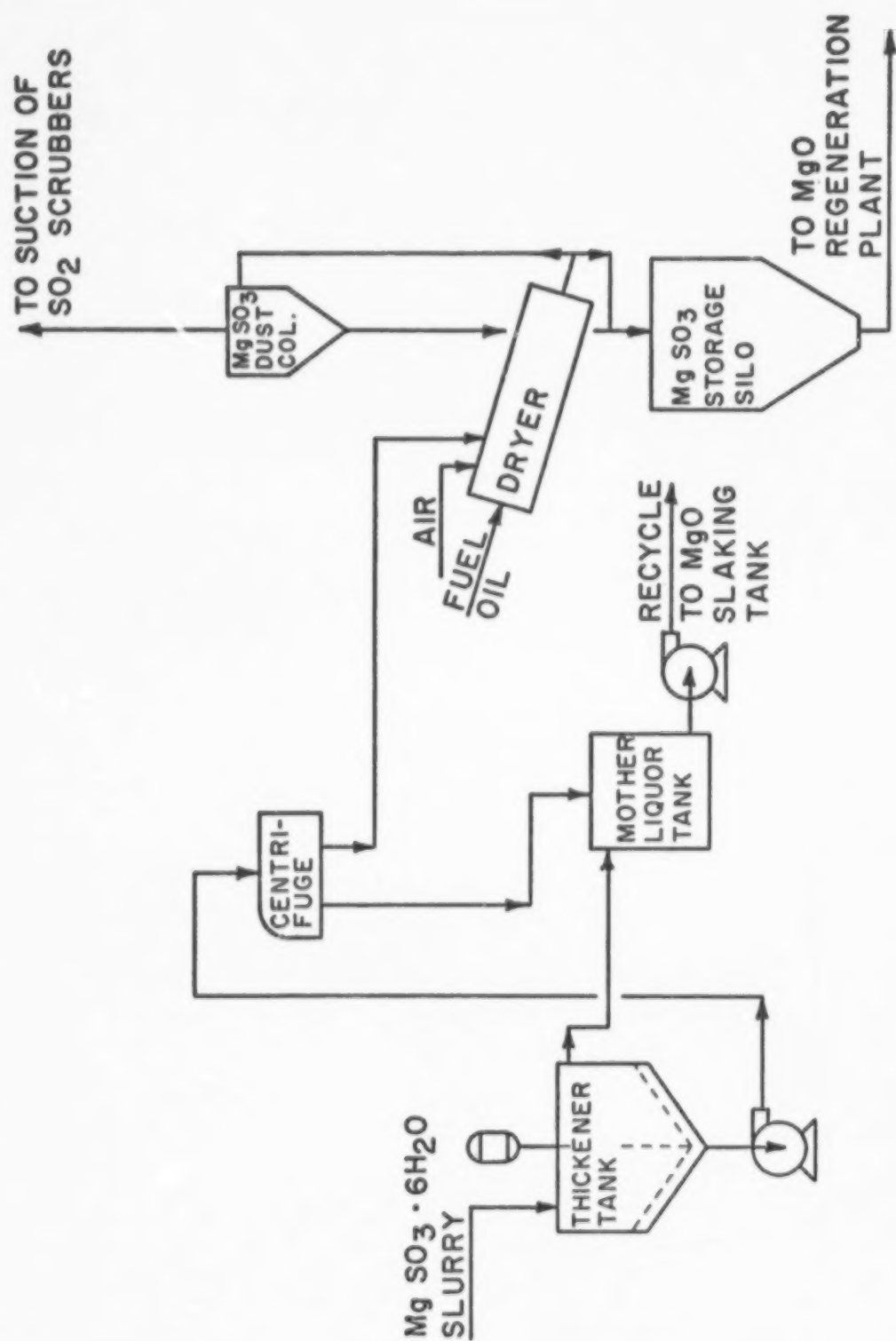


Figure 3. SO_2 scrubbing system - Mg SO_3 recovery.

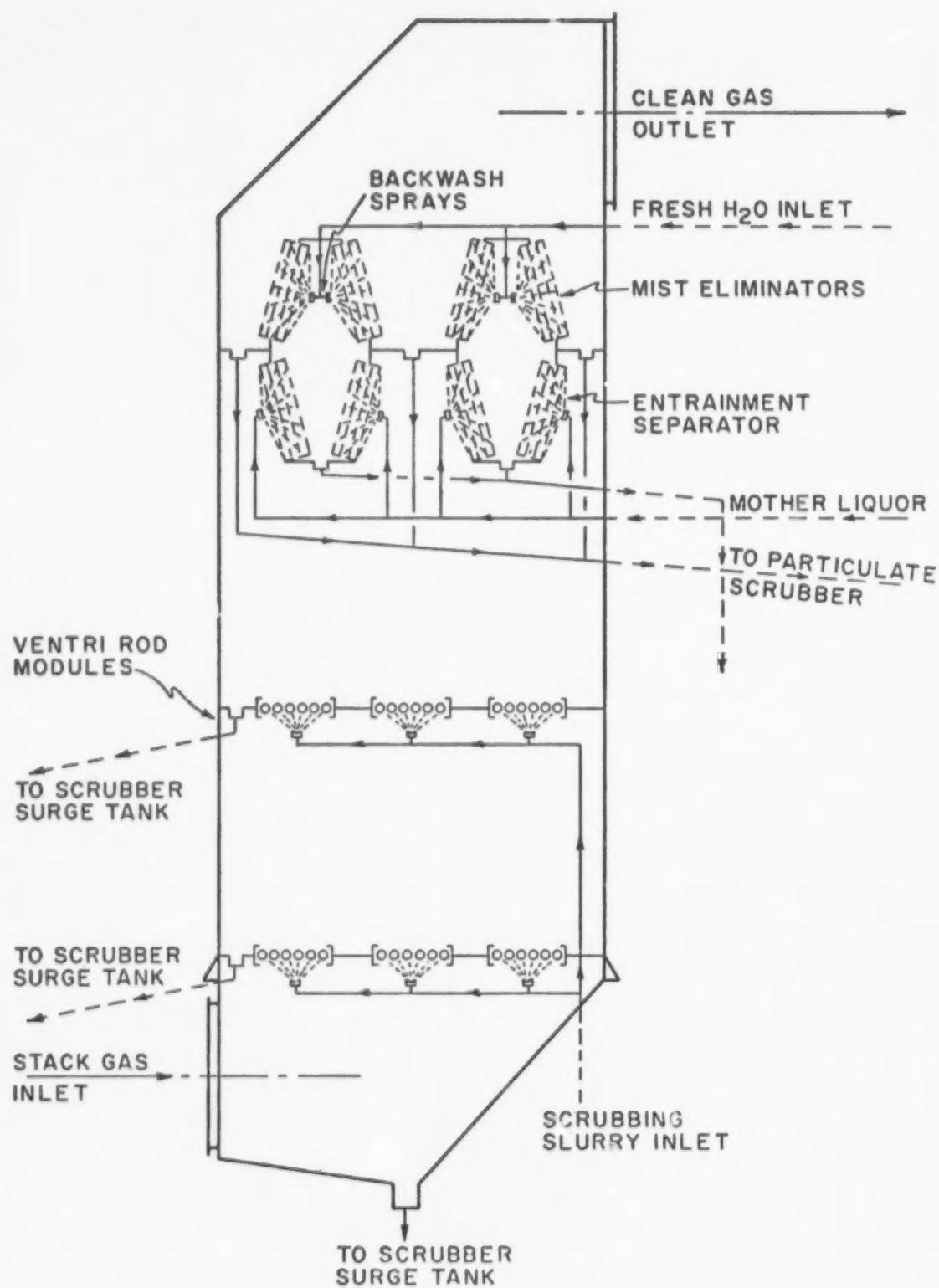


Figure 4. SO_2 scrubber unit detail.

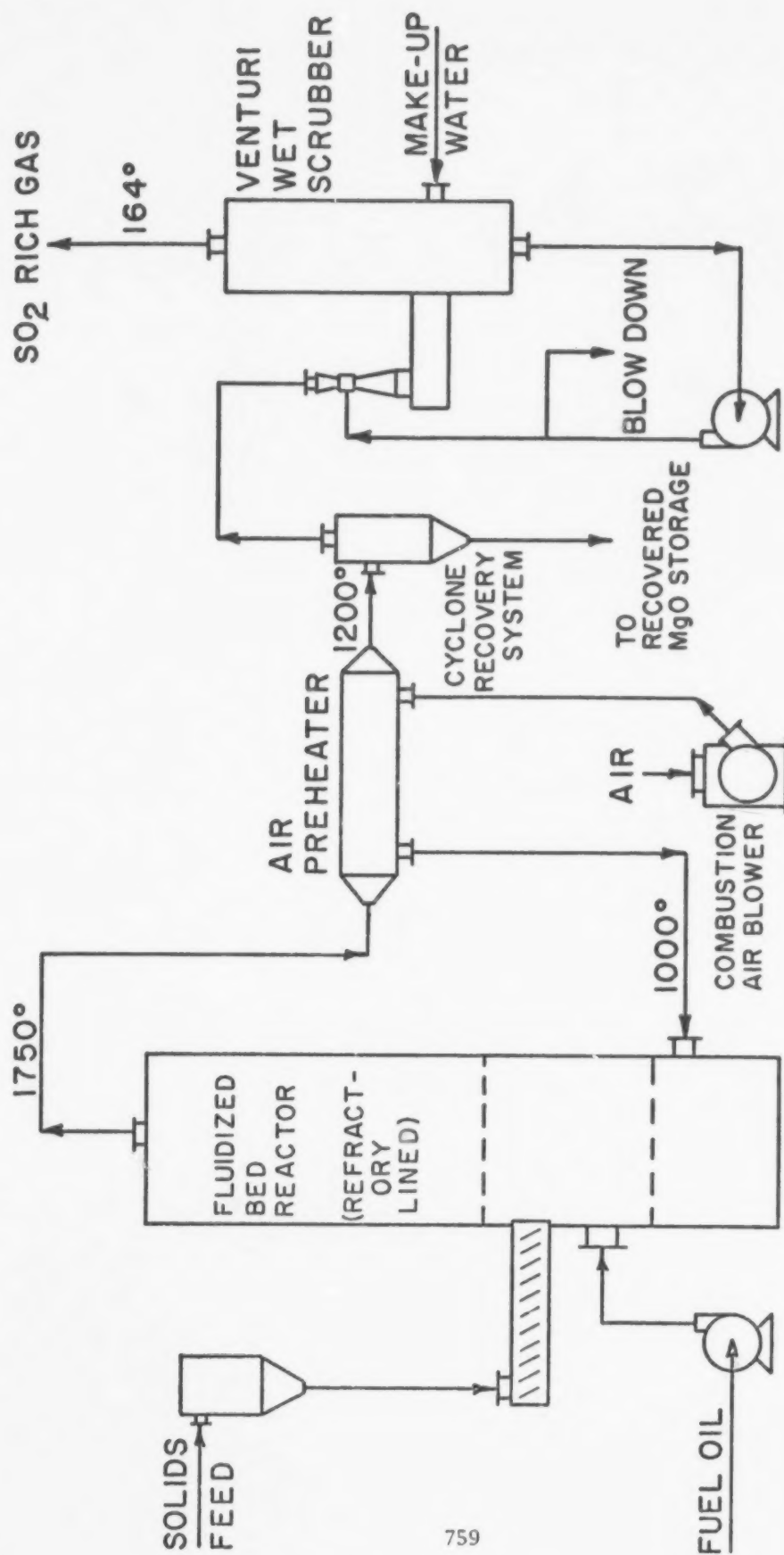


Figure 5. MgO regeneration plant.

INTERIM REPORT ON CHIYODA THOROUGHbred 101
COAL APPLICATION PLANT AT GULF POWER'S SCHOLZ PLANT

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ABSTRACT

This paper presents a summary of the operating experience during 1975 of Chiyoda International Corporation's 23 megawatt flue gas desulfurization plant at Gulf Power Company's Scholz Steam Plant. Emphasis is placed on system availability, chemical consumptions, solid and liquid waste disposal, mechanical problems and their resolution, and planned future testing. Also included is an appendix showing construction costs and utility and chemicals consumptions for a hypothetical 500 megawatt FGD facility. Testing and evaluation of the Scholz Plant are under the direction of Southern Services, Inc.

INTERIM REPORT ON CHIYODA THOROUGHbred 101
COAL APPLICATION PLANT AT GULF POWER COMPANY'S SCHOLZ PLANT

I. INTRODUCTION

The Chiyoda THOROUGHbred 101 (CT-101) FGD system at Gulf Power Company's Scholz Plant in Sneads, Florida has now completed its first ten months since initial startup in February, 1975. As Chiyoda's first FGD plant in the U.S. and its first to operate on a coal fired boiler, this CT-101 is both a demonstration and a testing facility.

The technical capabilities of this process have been well demonstrated by the thirteen commercial FGD systems currently scrubbing stack gases from oil fired boilers in Japan. The first of these plants, which range up to 350 mw, came on line in November, 1972, and the most recent in October, 1975. (Table 1). Initial operations of these plants were reported previously in the literature. (1,2)

At the Scholz Power Plant emphasis is on testing the performance of CT-101 on scrubbing flue gases generated from a coal fired boiler, for comparison with the performance on oil generated flue gases in Japan. The testing and evaluation is being done under the direction of Southern Services, Inc. for the Southern Company (an electric utility holding company including Alabama Power Company, Georgia Power Company, Gulf Power Company, Mississippi Power Company, Southern Electric Generating Company, and Southern Services Inc.). This evaluation is part of a program to evaluate three prototype "2nd generation" flue gas desulfurization processes. This report presents the operating experiences of Chiyoda's facility during 1975.

II. PROCESS DESCRIPTION

The 23 mw capacity of the desulfurization unit corresponds to approximately one-half of the rated boiler capacity. The design basis of the CT-101 at the Scholz Plant is shown in Table 2. At 100% of design basis the plant consumptions are: 1800 lb/hr limestone, 60 gpm water (excluding recyclable cooling water), 50 gal/hr No. 2 fuel oil (reheat to 300°F), 50 lb/hr catalyst, and 1200 kw.

The process has four basic operations (refer to Figure 1):

- 1) Prescrubbing
- 2) Absorbing
- 3) Crystallizing
- 4) By-product/waste handling

TABLE 1 THE CHIYODA THOROUGHRED 101 FLUE GAS DESULFURIZATION PLANTS

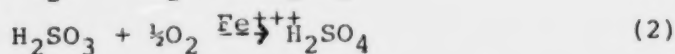
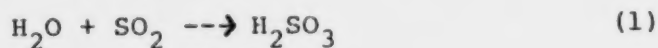
<u>Owner of Plant</u>	<u>Location</u>	<u>Capacity (scfm)</u>	<u>Capacity (MW)</u>	<u>Avail- ability</u>	<u>Period of Availability</u>
Nippon Mining	Mizushima	20,800	-	95%	May '73 to Dec. '75
Fuji Kosan	Kainan	98,000	-	97%	May '73 to "
Mitsubishi Rayon	Otake	56,000	30	97%	May '73 to "
Tohoku Oil	Sendai	8,800	-	100%	June '73 to "
Daicel	Aboshi	62,000	33	96%	Dec. '73 to "
Amagasaki Cokes	Hyogo	15,500	-	97%	July '74 to "
Hokuriku Electric Power	Toyama	466,000	250	100%	Oct. '74 to "
Mitsubishi Chemical Ind.	Yokkaichi	250,000	135	94%	July '74 to "
Mitsubishi Petrochemical	Yokkaichi	93,000	50	99%	Dec. '74 to "
Mitsubishi Petrochemical	Kawajiri	435,000	235	100%	Dec. '74 to "
Denki Kagaku Kogyo	Chiba	75,000	40	100%	June '75 to "
Hokuriku Electric Power	Fukui	650,000	350	100%	June '75 to "
Toyama Cooperative Power	Toyama	466,000	250	100%	Sept. '75 to "

Table 2 SUMMARY OF DESIGN AND OPERATING CONDITIONS - CT-101 FACILITY AT THE SCHOLZ PLANT

Conditions		Design	Operating Range	Typical Values	Future Conditions
Gas Rate, scfm		53,000 81,000 acfm @ 350°F	20,000-55,000	35,000-45,000	40,000-50,000
SO ₂ Loading, ppm					
Inlet		2250	800-2000	1000-1300	2000-3500
Outlet		225	50-250	90-150	
SO ₂ Removal, %		90	80-95	82-87	
Particulate Loading, gr/scf					
Inlet		0.1	---	---	1.0
Outlet		0.01	---	---	0.02
Particulate Removal, %		90	---	---	98
O ₂ , %		3.0	6-10	7-9	
H ₂ O, %		9.0	---	---	
Excess air, %		20.0	---	---	
Fuel					
Sulfur content, %		3.0	1.7-2.5	1.7 & 2.2 ^a	
HHV, BTU/lb		12,200	11,700-13,100	12,500	
Ash content, %		14	10.6-13.7	12.3	
Bottom Ash, %		15	---	---	
Limestone					
Purity, % CaCO ₃		98	93-95	94	
Max. % MgCO ₃		2	1-1.9	1.3	
Min. Particle Size, % 200 mesh		90 ^b	66-84 ^c	76 ^c	a. 1.7 during 2/75 through 7/75 2.2 during 9/75 through 12/75 b. wet sieve analysis c. dry sieve analysis
Catalyst % Fe ⁺⁺⁺			7.8-10.7	10.0	

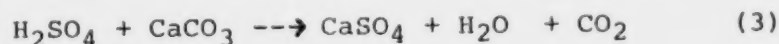
The prescrubber section is responsible for cooling the incoming flue gas to its saturation temperature and for scrubbing out fly ash and chlorides. The suspended solids concentration in the prescrubber recycle liquid is controlled by an intermittent discharge of settled ash from a thickener.

Sulfur dioxide is removed via counter current scrubbing with weak sulfuric acid in the fixed bed absorber. The absorption of SO_2 by H_2O gives sulfurous acid (H_2SO_3) which is catalytically oxidized by ferric ion to H_2SO_4 in the oxidizer. (Equations 1, 2).



This scrubbing liquid is not saturated in calcium sulfate, obviating scaling in the absorber/oxidizer or mist eliminator. The flue gas then passes through a two rank chevron type mist eliminator before reheat is added, and exits through a local test stack. This mist eliminator has never been washed and pressure drops are consistently less than 0.2 inch H_2O .

The concentration of sulfuric acid in the scrubbing liquid is maintained at about 2.0 wt% by continuous withdrawal of absorbent to the crystallizer. In the crystallizer, this absorbent is partially neutralized to about 1.0 wt% H_2SO_4 by limestone, the reaction product being gypsum crystals. (Equation 3).



Gypsum is removed from the system by a continuous screw decanter type centrifuge as an 80-88% solids cake. This solid by-product is currently being held in a dry pond. The overflow from the crystallizer and underflow from the centrifuge pass to a clarifier where small gypsum crystals settle out and are returned as seed crystals to the crystallizer. Overflow from the clarifier is essentially free of suspended solids and is returned to the absorber as mother liquor.

There are two waste streams in the system presently. One is fly ash bleed from the prescrubber section and the other is a mother liquor bleed from the crystallization section for water balance and for control of the chloride concentration in the absorbent. Maintaining chloride concentrations in the absorption/crystallization section below 200 ppm is presently necessary in the CT-101 process at Scholz to prevent pitting corrosion in the stainless steel vessels. These two waste streams are combined, neutralized by limestone, and discharged to a wet pond for removal of suspended solids before overflow into the plant ash pond.

III. EXPERIENCE

A. Availability

Availability as defined here is the hours of scrubber operation divided by hours of boiler availability to the scrubber, times 100. Table 3 shows the periods of plant operation and the reasons for outages since initial startup with flue gas in February, 1975. The first few months shakedown period was characterized by many small problems resulting in a very low availability (30% February - May). Many of these problems were resolved by June, and availability during June and July was somewhat improved (84%) but still below expectations. Many of these early outages were perhaps longer than would normally be the case, because the maintenance crew was overburdened and working with new equipment and a new process. Additionally, occasional delays in repair occurred while the exact nature of a problem was investigated by Chiyoda engineers and manufacturers' representatives. In early July, a separate maintenance contract was issued to increase the available maintenance forces for the FGD systems and, in general, repairs were completed more quickly. The six-week outage starting in August was the result of unbalancing of the centrifuges. After repair of the centrifuges and installation on September 15, the availability through December, 1975 averaged above 97%.

B. Equipment

During the shutdown of August and September most of the vessels and rotating equipment were inspected. These inspections verified that there was no scaling or plugging in the absorber, oxidizer or mist eliminator. The crystallizer showed some settled solids on the bottom but no evidence of scaling.

The unbalancing of the centrifuge is primarily caused by a high non-uniform wear rate on the screw, and this continues to be a problem. The Stellite No. 1 hard facing on the screw conveyors is wearing much faster than experiences in Japan predicted, although one unit has now operated continuously for four months without becoming unbalanced. It appears that this relatively long run without failure is due to even wearing of the conveyor screw, thereby avoiding unbalancing. Previously, one centrifuge became unbalanced after only six weeks operation, but this may have been an anomalous case. Hardness testing on one conveyor showed that the Stellite No. 1 facing hardness was less than that of the stainless steel conveyor. The reason for this may be that the technique for applying the facing is different from that in Japan. As a

Table 3 OPERATION HISTORY

in operation*		Outage Hours	Cause of Outages & Remarks**	
'75				
F			Feb. 11	Initial catalyst charge
E			12	Crack in FRP oxidizer vessel, additional
B		387.33		mats glued.
M				
A			March 11	Modification of Waste Disposal. Waste
R				neutralization moved to pond from plant
C		342.75		site. The move was necessitated by insuf-
H				ficient capacity of the disposal pump and
				by scaling in the discharge line.
A		241.00	April 3	Prescrubber shell flange leakage; bolts
P				tightened.
R		15.00	18	FRP line leakage
I				
L		500.17	21	Flue gas blower inlet vane broken.
				Replaced corroded S.S. parts in Prescrubber
				area with corrosion resistant material.
M				
A			May 15	Prescrubber FRP lined nozzle developed a
Y		442.23		pinhole leak. Leakage on FRP piping of
				pump discharge. Checked oxidizer feed
				pump bearing, thought to be over heating
				(major reason for outage), instrument air
				compressor alignment & oxidizing air in-
				strumentation.
J				
U				
N				
E				
J		71.58	July 6	Limestone feeder jammed by 7/8" nut,
U				inadvertently entered with limestone powder
L				
Y		34.15	21	FRP pipe leakage on Prescrubber.
		14.00	28	One centrifuge unbalanced.
A				
U		1044.22	Aug. 3	Both centrifuges unbalanced; shipped to
G				a machinery in Pensacola which failed to
				repair and sent to the manufacturer in
				Houston.

Table 3 OPERATION HISTORY
(continued)

'75 S E P T			
	47.0	Sept. 23	Sump pump misalignment; changed to spare pump
O C T			
N O V	0.67	Nov. 10	Flue gas blower inlet vane broken; removed broken vane.
	0.17	24	Prescrubber FRP lined nozzle pinhole; welded from outside.
D E C	0.33	Dec. 8	ditto
	1:5	18	ditto
	1:3	20	ditto
	14.7	26	Prescrubber nozzle lining repaired from inside.
			Total system availability, including shakedown period, February 11, 1975 through December 31, 1975, was 60%.

* Shaded area indicates period of operation.

** Occasionally after extended outages, there were problems with the balancing of the F.D. fan when starting up. These problems were due to corrosion of the carbon steel and the fan impeller, most likely caused by leakage of hot flue gas around the isolation damper. Delays in startup due to rebalancing of the fan are not listed as the cause of outage, but are included in the outage hours.

result of these findings, new hard facing materials have been investigated in the event that the performance of the current one cannot be improved. Depending on the results of these investigations, a new facing material may be used when re-facing is next required. It should be noted that, while the use of centrifuges is not unique to the Scholz facility, in its large FGD plants Chiyoda usually uses less troublesome basket centrifuges or vacuum filters.

There have been few pump problems during the year. Plant operation stopped once in September due to a failure of the disposal pump which did not have a standby spare. The pump was corroded due to inadequate sealing and flushing. Pump problems not causing process upsets include unbalancing of the impeller in the absorber/oxidizer recirculation pump, tripping of the limestone slurry pump due to excessive slurry concentration, and breakage and slippage of drive belts. The unbalancing of the oxidizer pump impeller was due to a defect in the rubber liner and subsequent corrosion. The belts are being changed to polybelts in an attempt to improve operating life.

Other equipment problems include occasional jamming of the limestone feeder by "tramp" metal from the silo, and leakage from the flanges on the FRP duct between the prescrubber, absorber, and mist eliminator. There have been many leakage problems with the FRP used in the plant, usually attributable to excessive vibration, inadequate bracing, or poor installation.

C. Instruments

Instrument problems have been few, but irksome. Most notably, the prescrubber level transmitter and the limestone and gypsum slurry analyzers have been unreliable. The problems with the level transmitter have been traced to an improper gasket material on the sealed system, and have now been resolved. The limestone slurry analyzer was a differential pressure type intended to provide only a rough indication of concentration but did not perform properly because of mis-specified components. It is now working after modifications. The gypsum slurry analyzer was an ultrasonic unit which failed during the first three months of operation due to erosion of the probes and has not been used since. The slurry analyzer problems were easily circumvented by manual observation and measurement, although this action has not allowed optimal operation.

D. Process

1. Sulfur Dioxide Removal

Correlations of SO₂ removal efficiencies with process parameters have been thoroughly investigated in Japan during the course of development and commercial operations, and the optimal operating conditions are well defined. Due to the long shakedown period and the fact that the Gulf Power operators were learning three FGD systems simultaneously, operating conditions have been maintained within loose guidelines rather than at specified setpoints. As a result, process performance has occasionally been below design specifications. During periods of proper operation it has generally equalled design specifications.

Throughout most of 1975 only relatively low sulfur coal was available at the Scholz Plant, and typical inlet SO₂ concentrations were 1000-1300 ppm. SO₂ removal efficiencies have ranged from 80-95%, depending on inlet SO₂ loading, absorbent concentration, and L/G. Performance in December of 1975 showed SO₂ removal efficiencies of about 82% overall. However, SO₂ removal efficiency data obtained to date disagree with Chiyoda observations and this discrepancy is being investigated. The outlet SO₂ analyzer in particular has given intermittent problems, and is suspected to be the cause of these differences. The result of this investigation will be reported in the future.

2. Particulates and Chlorides Removal

The prescrubber section was designed to remove fly ash and chlorides from the flue gas before it enters the absorber. Normal inlet particulate concentrations have been quite low, however, adequate testing has not been done to verify actual values. Testing to determine chloride removal has been performed, but the results are inconclusive. Further tests will be conducted in the future in an attempt to determine accurate particulate and chloride removals.

3. Limestone Utilization

Material balance and solids analyses generally indicate a 98-99% calcium utilization, although some individual results indicate utilizations as low as 96%. The limestone particle size used at the Scholz facility is of a larger mesh size than specified (76% < 200 mesh instead of 95% < 200 mesh), and it was

suspected that this would give a lower than normal utilization. The fact that utilization has not decreased may reflect differences in particle size analysis which is done by dry sieve at the Scholz Plant, while Japan experiences are based on a wet sieve analysis. A small amount of unreacted limestone in the gypsum product is useful to neutralize residual acid in the 10-15% moisture carried with the dry gypsum. The limestone used at the Scholz Plant comes from the Alabaster area near Birmingham.

4. By-product Disposal

Liquid Waste. As the plant is currently operating, it is not a closed loop. The discharge is approximately 20 gpm, and disposal of acidic water poses a problem. At the present time, this water is neutralized with limestone, then sent to a lined settling pond where fly ash, gypsum, unreacted limestone, and $\text{Fe}(\text{OH})_3$ (catalyst from mother liquor bleed) settle out.

The overflow from the settling pond has been sampled and analyzed monthly since July, 1975. The analyses, as shown in Table 4, include trace elements as well as major constituents. Concentrations of total dissolved solids, iron, mercury, and fluoride in excess of state water quality standards for receiving waters have been measured in the settling pond overflow. Selenium concentrations in excess of U.S.P.H.S. Drinking Water Standards have also been measured in this overflow. However, the settling pond overflow is routed to the Scholz Plant ash pond which ultimately discharges to the Apalachicola River where state water quality standards are applicable, and it is important to realize that there have been no violations of state water quality standards, as determined by monthly monitoring of the ash pond overflow.

At a full-scale installation, it is likely that treatment and/or reduction of the liquid waste will be required by both state and federal regulations. Treatment could be accomplished by evaporation if the volume of waste is reduced. Serious consideration is currently being given by the EPA to demonstrating vapor compression evaporation on the Chiyoda liquid waste at the Scholz Plant. Plans to reduce water consumption and the liquid waste stream and approach a closed loop are being implemented as described below.

Table 4 CIC EFFLUENT ANALYSES - JULY-DECEMBER 1975

Paremeter (Units)	Liquid Purge Settling Pond Overflow	Gypsum Pond Underdrain	State of Florida Water Quality Standards (1)
Total Dissolved Solids (mg/l)	2000-4994 (2)	2250-2754 (2)	500 (3)
Total Suspended Solids (mg/l)	6-393 (4)	<1-4	---
pH (Standard Units)	2.3-7.5 (2)	6.8-7.2	6-8.5
Conductivity (Micromhos/cm)	3050-6700	2000-2670	500
Temperature (°F)	47-85	55-88	---
Total Calcium (mg/l as Ca)	330-1100	540-644	---
Total Magnesium (mg/l as Mg)	39-246	14-87	---
Total Sodium (mg/l as Na)	28-65	12-67	---
Total Potassium (mg/l as K)	0.85-2.93	0.47-1.65	---
Total Hardness (mg/l as CaCO ₃)	1093-3360	1406-1830	---
Total Phosphorus (mg/l as P)	<0.01-0.036	<0.01	---
Dissolved Silica (mg/l as SiO ₂)	12-31	1.5-2.3	---
Sulfate (mg/l as SO ₄ ⁼)	1160-2750 (5)	1370-1650 (5)	---
Sulfite (mg/l as SO ₃ ⁼)	<1	<1	---
Carbonate (mg/l as CaCO ₃)	0	0	---
Bicarbonate (mg/l as CaCO ₃)	0-38	35-44	---
Hydroxide (mg/l as CaCO ₃)	0	0	---
Chloride (mg/l as Cl)	51-138	2.3-9.1	250

Table 4 CIC EFFLUENT ANALYSES - JULY-DECEMBER, 1975
(continued)

Paremeter (Units)	Liquid Purge Settling Pond Overflow	Gypsum Pond Underdrain	State of Florida Water Quality Standards (1)
Carbon Dioxide (mg/l as CO ₂)	25-970	4.8-12.0	---
Total Acidity (mg/l as CaCO ₃)	0-1080	0	---
Color (Standard Units)	0.5-13	0.5-8	---
Turbidity (NTU)	4.2-92.0 ⁽²⁾	0.18-1.6	50
Total Aluminum (mg/l as Al)	2.10-4.80	<0.05-0.24	---
Total Arsenic (mg/l as As)	<0.01	<0.01	0.05
Total Cadmium (mg/l as Cd)	<0.01	<0.01	---
Total Chromium (mg/l as Cr)	<0.01-0.04	<0.01	0.05 ⁽⁷⁾
Total Copper (mg/l as Cu)	0.06-0.60 ⁽²⁾	<0.01	0.5
Total Iron (mg/l as Fe)	0.54-109.0 ⁽²⁾	0.019-0.17	0.3
Total Lead (mg/l as Pb)	<0.01	<0.01	0.05
Total Manganese (mg/l as Mn)	0.17-1.08 ⁽¹¹⁾	<0.01-0.32 ⁽¹¹⁾	---
Total Mercury (mg/l as Hg)	<0.0002-0.0068 ⁽²⁾	<0.0002-0.0004	ND ⁽⁸⁾
Total Nickel (mg/l as Ni)	0.02-0.15	<0.01	---
Total Selenium (mg/l as Se)	0.016-0.13 ⁽⁹⁾	<0.002-0.04	---
Total Zinc (mg/l as Zn)	0.26-1.3 ⁽²⁾	<0.01	1.0
Oil and Grease (mg/l)	<1	<1	15

Table 4 CIC EFFLUENT ANALYSES - JULY-DECEMBER, 1975
(continued)

Parameter (Units)	Liquid Purge Settling Pond Overflow	Gypsum Pond Underdrain	State of Florida Water Quality Standards (1)
Nitrate (mg/l as N)	20-105 ⁽¹⁰⁾	4-43	---
Chemical Oxygen Demand (mg/l)	<1-11	<1-4.9	---
Fluoride (mg/l as F)	4.2-27 ⁽²⁾	0.54-0.94	1.4-1.6 ⁽⁶⁾
Boron (mg/l as B)	1.0-4.6 ⁽¹²⁾	<0.1	---

- (1) Applicable to receiving waters only after reasonable opportunity for mixing with wastes has been afforded.
- (2) These values would violate water quality standards if mixing were not taken into account.
- (3) As a monthly average: 1000 mg/l instantaneous.
- (4) The EPA effluent guidelines for stream electric power plants for TSS is 100 mg/l maximum for any one day and 30 mg/l for a monthly average.
- (5) The USPHS (1962) Drinking Water Standard for sulfate is 250 mg/l.
- (6) Applicable only to waters used for sources of Class 1 water supply; for other waters, the standard for fluoride is 10 mg/l.
- (7) For total chromium; for total chromium in the effluent discharge, the standard is 1.0 mg/l; for hexavalent chromium in the effluent discharge, the standard is 0.5 mg/l.
- (8) None detectable (for practice purposes at this time, ND= <0.0002 mg/l).
- (9) The USPHS (1962) Drinking Water Standard for selenium is 0.01 mg/l.
- (10) The USPHS (1962) Drinking Water Standard for nitrate is 45 mg/l.
- (11) The USPHS (1962) Drinking Water Standard for manganese is 0.05 mg/l.
- (12) The EPA proposed water quality criteria for public water supply intake (October 1973) for boron is 1.0 mg/l.

By-product Gypsum. The gypsum produced at the Scholz Plant consists almost entirely of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). It is easily dewatered by centrifuging, and the solids content is typically 80-85%. The gypsum has been physically characterized using three soil tests, grain size analysis, consolidation, and Atterberg limits. The grain size analysis indicates that the Chiyoda gypsum is composed of 28% sand size, 66% silt size, and 6% clay size material (MIT classification system). The majority of the gypsum particles ranged in size from 0.01 mm to 0.1 mm. From consolidation tests, it was learned that landfilled Chiyoda gypsum could support significant loads without appreciable settlement. However, loads subject to vibration could not be placed on a gypsum landfill because the gypsum tends to liquify with vibration if the water content of the gypsum does not remain low (approximately 15% or less). A range of permeabilities was calculated from the consolidation tests to be 10^{-6} - 10^{-5} cm/sec. Atterberg limits testing revealed that the Chiyoda gypsum is non-plastic and that it will liquify when it is both wet and subjected to vibration.

Currently the gypsum is being disposed in a lined pond equipped with an underdrain. Rain water percolated through the gypsum, passes through the underdrain, and is routed to the ash pond. The water from the underdrain has been sampled monthly since July, 1975, and the results of the analyses are shown in Table 4. In general, with the possible exception of total dissolved solids, it appears that this water (leachate) poses no water quality problems. This is to be expected, because almost all trace contaminants contained in the flue gas are removed in the prescrubber. The liquid waste from the prescrubber is neutralized and routed to the settling pond as described earlier.

IV. FUTURE PLANS

A. Reliability Testing

A six month performance reliability test will be completed at the end of March, 1976. The final testing to be done during this period will include continuing material balance checks and ability of the process to follow load fluctuations. Additional tests will also be conducted on particulate and chloride removal capabilities of the prescrubber.

B. Testing with Various Coals

As the Scholz facility is a proving ground for CT-101 applicability to coal generated flue gas, tests related to variations in coal are being undertaken. The present Southern Company test program is scheduled to end in June. However, during the next one or two years, the plant will continue operation with different coals, permitting further testing by Chiyoda of higher sulfur and possibly higher ash coals.

C. Reduction of Clear Water Consumption

As mentioned earlier, there are two liquid waste streams within the plant, one from the prescrubber and the other from the mother liquor for controlling chloride concentrations and for water balance. Present plans are to reduce these streams and approach closed-loop operation. The design of the precooler (saturator) in the prescrubber calls for a flow rate of clear water equal to twice the rate of evaporation. The excess water is intended to prevent scaling in the precooler and to convey fly ash. Inspection of prescrubber conditions indicates that all of this excess water is not necessary to prevent scaling and may be eliminated. In addition, clear water is being used in preparation of the limestone slurry, and this water has been responsible for half of the mother liquor bleed for water balance; the remaining half comes from pump seal water which cannot be eliminated.

The objective of the water saving plan is to demonstrate the reduction in the volume of liquid waste accomplished by utilizing mother liquor as make-up water to the limestone slurry tank and as the conveying medium for fly ash bleed from the prescrubber (refer to Figure 2).

The addition of mother liquor to the limestone slurry tank will eliminate the use of clear water there, should obviate bleeding mother liquor to maintain the water balance, and will retain some ferric ion catalyst currently being lost in the bleed stream. On the other hand, sufficient mother liquor must be bled to the prescrubber to maintain the chloride concentration in the absorption/crystallization section below 200 ppm. Figure 3 shows the required mother liquor bleed rate to the prescrubber as function of chloride content of the coal and the chloride removal in the prescrubber. The addition of mother liquor to the prescrubber and to the limestone slurry has already been successfully implemented at a chemical company in Japan but will still be carefully monitored at the Scholz Plant.

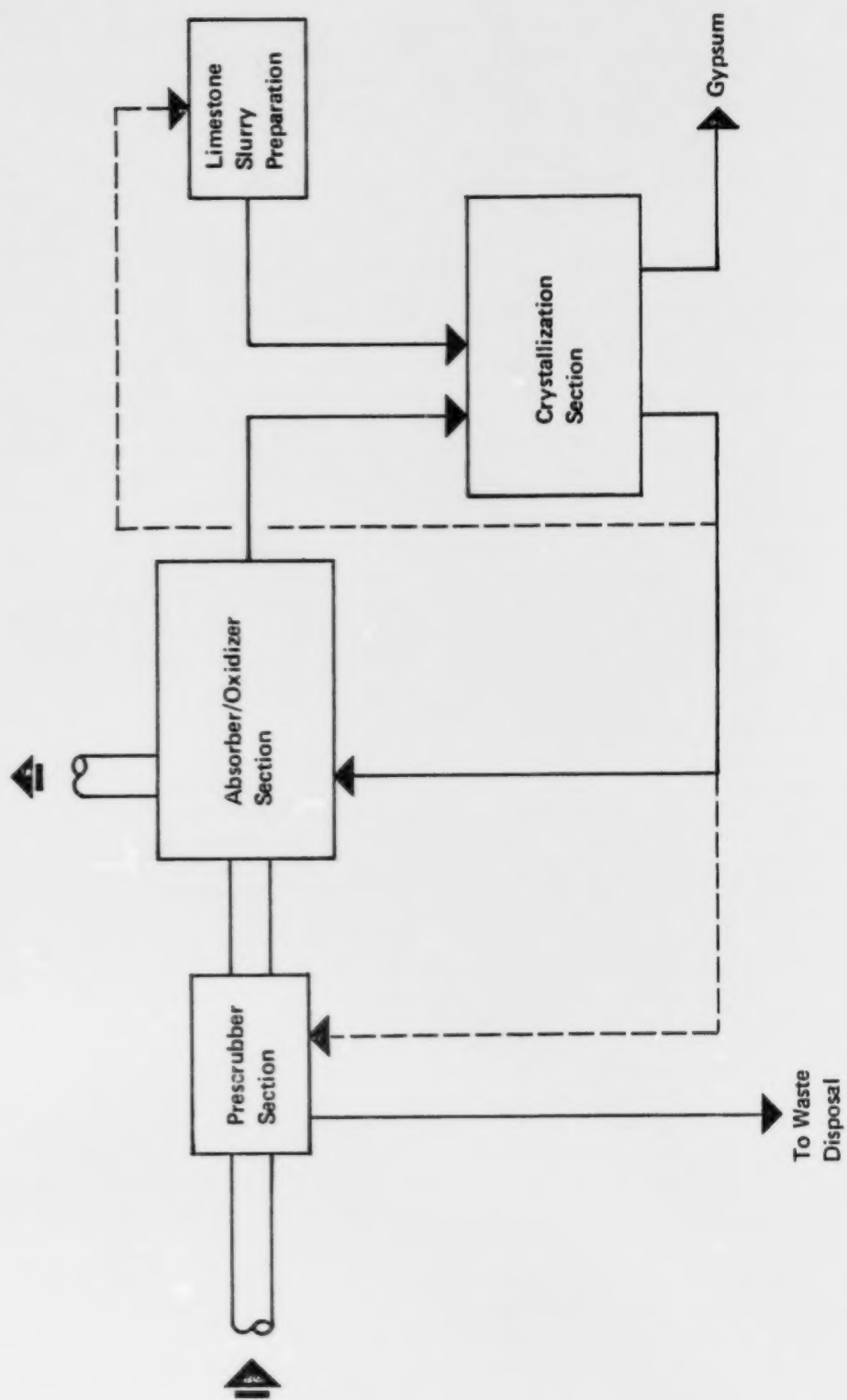
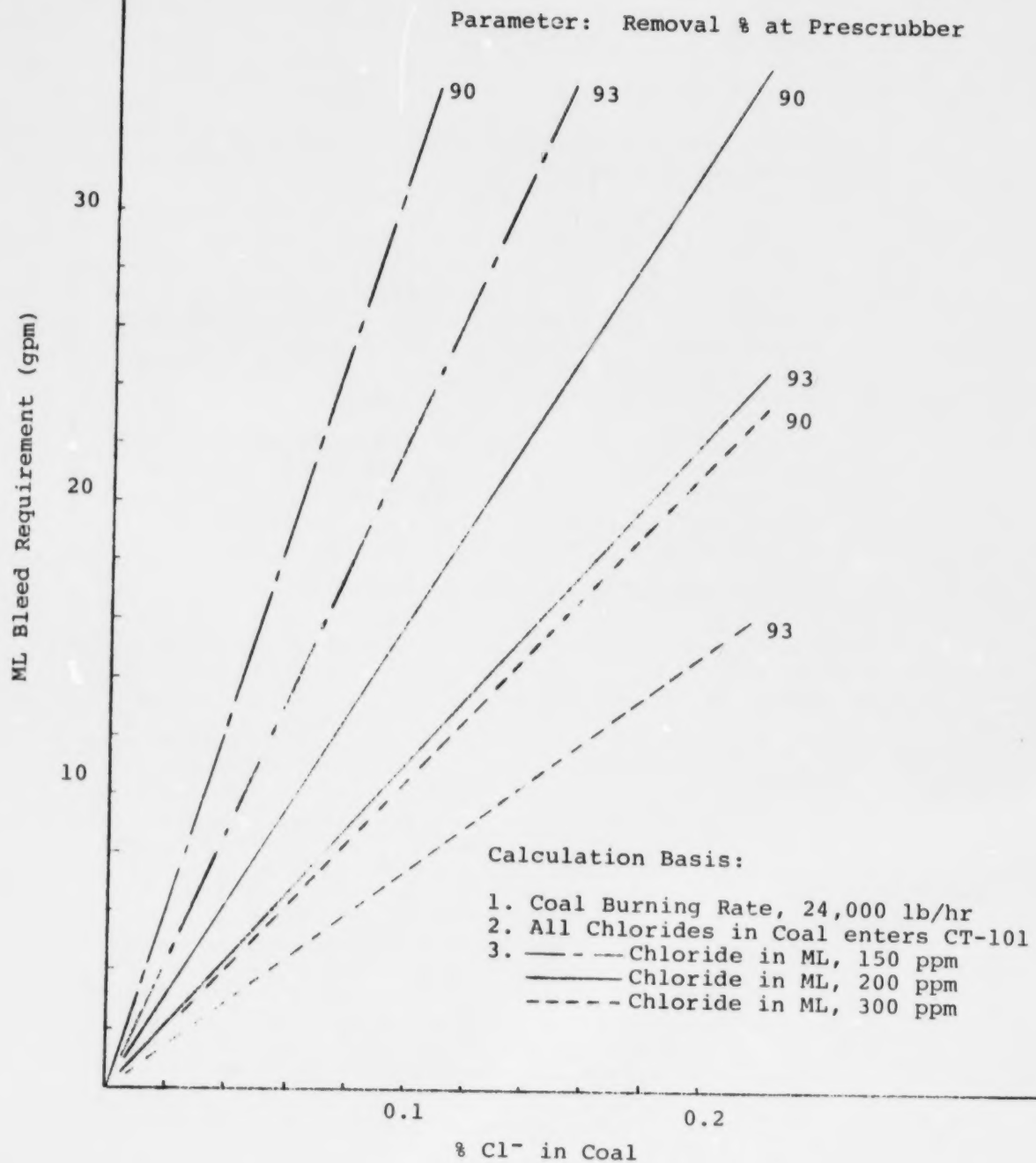


Figure 2 Block flow diagram indicating water saving plan (dotted lines)

Figure 3 Mother Liquor Bleed
vs
Chloride in Coal



Chiyoda's laboratories have also noted that NO_3 ion in solution is an inhibitor to pitting corrosion by chlorides. Nitrogen oxides are absorbed in the CT-101 up to a saturation limit, and if the concentration of NO_3 is sufficient, the maximum permissible concentration of chloride may increase significantly, thus permitting further reduction of the bleed rate to the prescrubber (if the water balance permits). The final process blowdown from the facility is expected to be 10 gpm or less.

D. Implementation Schedule

Testing of the water saving plan, which will be initiated after completion of the six month reliability test, calls first for addition of mother liquor to the prescrubber and the limestone slurry preparation system. Limestone slurry will be prepared exclusively from mother liquor and the effect on slurry preparation carefully monitored for a few months. Clear water will be used for cooling and saturating the incoming flue gas, and mother liquor will be added to the recycled scrubbing liquid for removal and discharge of fly ash and chloride.

A subsequent test will involve stopping all addition of clear water to the precoolers and using only recycled scrubbing liquid for both saturating and scrubbing incoming gas. In this mode, the waste discharged from the system will be minimized.

E. By-product Treatment and Utilization

As the gypsum is potentially a useful by-product and a waste problem, future testing will investigate both of these possibilities.

If total dissolved solids in the gypsum leachate pose a problem at a full-scale installation, leaching could be minimized by lining the disposal area or fixating the gypsum. The cost of conventional liners is high, so studies are underway at the Scholz Plant to test usage of compacted gypsum layer as a liner. Approximately one foot of gypsum will be placed in a 20' x 50' level area and will be compacted using conventional compaction equipment. Core samples of the compacted layer will be taken, and their permeability will be determined in the laboratory. Approximately three more feet of gypsum will be placed on top of the compacted layer, and the gypsum and gypsum liner will be allowed to weather. Core samples will be taken periodically to determine if liner permeability varies with time.

Chiyoda gypsum has been laboratory tested by a wallboard company and found to apparently be suitable for wallboard manufacture through small scale tests. A demonstration test using 100 tons of Chiyoda gypsum will soon be conducted at a wallboard plant in Jacksonville, Florida.

Agricultural use of gypsum as a calcium source for peanuts is fairly well established in the southeastern portion of the United States. Testing the suitability of the Chiyoda gypsum for agriculture began in December, 1975 with soil incubation studies at the University of Florida Agricultural Research Center in Quincy, Florida. The first month of soil incubation indicates that application rates up to twenty tons of Chiyoda gypsum per acre of soil will be feasible. The results of plant response tests will soon be available because test plants (peanuts and soybeans) were planted in soil-gypsum mixtures in early February, 1976.

The suitability of Chiyoda gypsum for cement production is being tested by a cement company. Preliminary observations indicate that Chiyoda gypsum can be used as a cement retarder. Results of these tests will be reported later.

All Chiyoda gypsum produced in Japan is sold to wallboard and cement manufacturers.

APPENDIX

This appendix, while it does not relate directly to Chiyoda's Scholz Plant, is included here to provide a realistic estimate of construction cost and utilities and chemical consumptions for a 500 MW FGD facility.

The process flow scheme for a 500 MW plant is the same as at Scholz except there would be two trains and a catalyst recovery section with the larger facility.

Table 5

CONSTRUCTION COST AND UTILITIES AND CHEMICALS CONSUMPTION FOR A HYPOTHETICAL 500 MW CAPACITY FGD FACILITY

Design Basis:

Gas Flowrate	1,120,900	scfm
Gas Temperature, inlet	310	°F
SO ₂ , inlet	2,200	ppmv
Particulates, inlet	0.1	grain/scf
Cl ⁻ in coal	0.1	wt. %
SO ₂ removal efficiency	90	%
Particulate removal efficiency	90	%
Reheated gas temperature	200	°F

Utility and Chemical Consumptions:

Power	17,000	KW
Make-up water	647	gpm
Recoverable cooling water	2,500	gpm
Limestone (as 100% CaCO ₃)	35	s-ton/hr
Catalyst (as 100% Fe ₂ (SO ₄) ₃)	100	lb/hr
Fuel oil for reheating	14	gpm
By-product Gypsum, including 12% Moisture	70	s-ton/hr
Waste Water	262	gpm
Construction Cost	\$38,000,000	

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1. Akiyoshi Tamaki, "Commercial Application of Dilute Sulfuric Acid Gypsum (The Chiyoda THOROUGHbred 101) Flue Gas Desulfurization Process for Large Power Plant Boilers", presented at the Sixty-Seventh Annual Meeting, American Institute of Chemical Engineers, December 4, 1974.
2. Masaaki Noguchi, "Status Report on the Chiyoda THOROUGHbred 101 Process", presented at United States Environmental Protection Agency, Flue Gas Desulfurization Symposium, November 4-7, 1974.

ADVANCED PROCESSES SESSION

Chairman: Archie V. Slack
President
SAS Corporation
Sheffield, Alabama

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STATUS AND ECONOMICS OF THE ATOMICS INTERNATIONAL
AQUEOUS CARBONATE FLUE GAS DESULFURIZATION PROCESS

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ABSTRACT

The Aqueous Carbonate Process (ACP) is an advance flue gas desulfurization process which produces elemental sulfur as its byproduct. The ACP system can be used for desulfurization of gases containing 200 to 20,000 ppm sulfur dioxide. Removal of SO_2 is accomplished in the ACP gas-treating subsystem, which is operationally decoupled from the regeneration subsystem. Either petroleum coke or coal is used as the reducing agent in the regeneration subsystem.

The decoupled nature of the process and the absence of recycle complications made it possible to adopt a stepwise approach to process development. All of the key process steps have been tested on the pilot plant scale, and the regeneration cycle has been proven by sequential operation of its individual steps. Extensive system engineering studies have been performed, and a proposal to design, build, and operate a 100 Mw ACP demonstration system has been prepared.

An economic evaluation of the ACP system has been performed by AI with the help of the Stack Gas Emission Studies staff of the TVA. The results of that evaluation indicate that ACP capital costs are competitive with other sulfur-producing FGD processes, and total annual operating costs are comparable to those of lime or limestone "throwaway" processes.

STATUS AND ECONOMICS OF THE ATOMICS INTERNATIONAL AQUEOUS CARBONATE FLUE GAS DESULFURIZATION PROCESS

INTRODUCTION

The Aqueous Carbonate Process (ACP) was conceived and developed as an advanced flue gas desulfurization (FGD) process with features that would solve or eliminate the problems encountered by first generation FGD processes. The features incorporated in the ACP system are summarized below:

- 1) Sodium carbonate solutions were selected as the desulfurization media in order to provide effective sulfur dioxide removal over wide concentration ranges.
- 2) The equipment chosen for the ACP gas-cleaning subsystem was selected on the basis of operational reliability and minimum maintenance requirements.
- 3) Potential problems associated with plugging, scaling, or other scrubber malfunctions were minimized, both by the nature of the scrubbing media and by the type of equipment selected.
- 4) For most applications, flue gas reheat requirements were eliminated.
- 5) The ACP gas-cleaning subsystem was designed to be decoupled from chemical regeneration steps and thereby become the sole operational interface with the flue gas source.
- 6) A sulfur-producing regeneration subsystem was provided in order to minimize the handling and/or disposal problems associated with the byproducts of the FGD process.

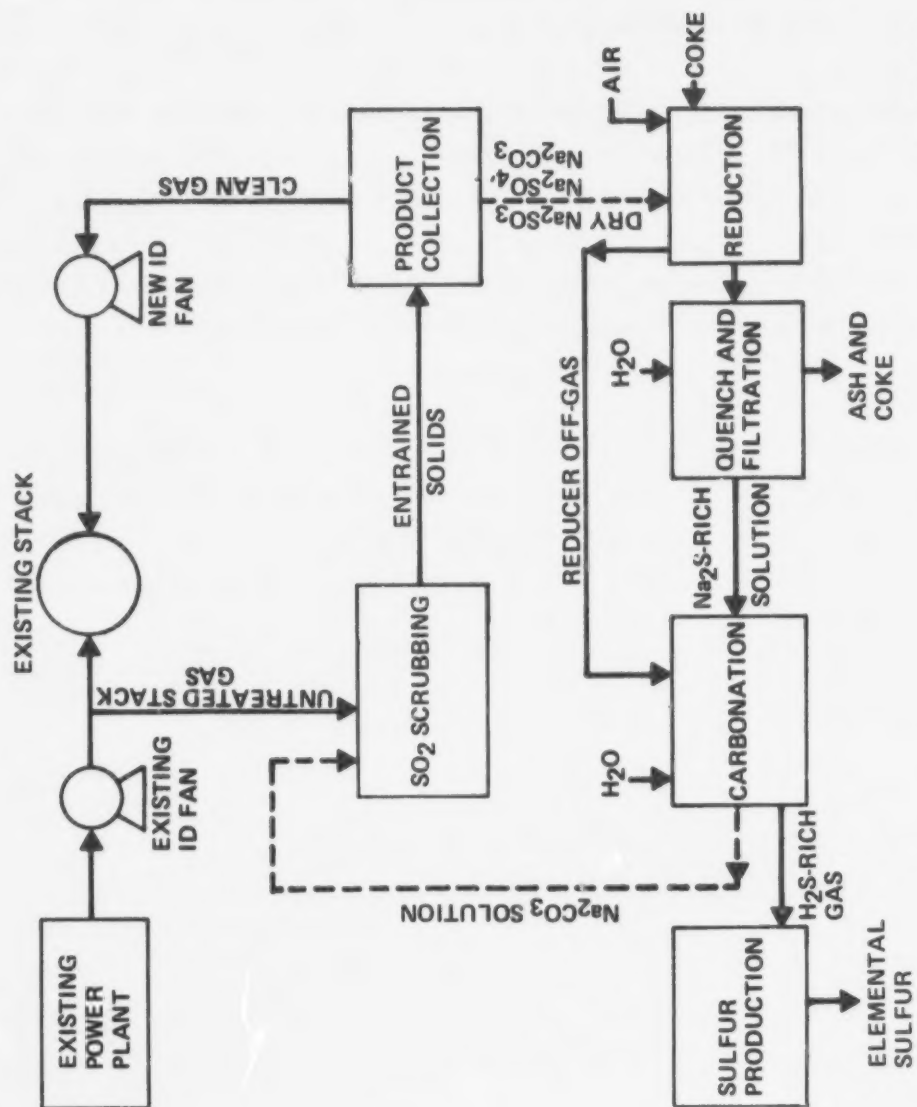
- 7) The ACP regeneration subsystem was designed to use a solid carbonaceous reducing agent (e.g., petroleum coke or coal) and thereby eliminate the need for natural gas or refined petroleum products.
- 8) Electrical requirements were minimized, and the need for other external energy sources, such as steam, were virtually eliminated.
- 9) Whenever technically feasible and economically justified, commercially available technology and/or equipment was selected for ACP use.

The ACP system has evolved in accordance with the above criteria and rationale. This paper describes how the system works and summarizes the process development work that has been done. The economics of the ACP system are also discussed, in terms of an evaluation performed by AI with the assistance of the TVA.

PROCESS DESCRIPTION

The six major process steps in the ACP are: (1) scrubbing, (2) product collection, (3) reduction, (4) quenching and filtration, (5) carbonation, and (6) sulfur production. Figure 1 is a block flow diagram showing these process steps as they would be assembled for an existing power plant application. The scrubbing and product collection steps are coupled by the gas stream that flows through the equipment; they make up the gas-cleaning subsystem.

The dashed lines in Figure 1 emphasize the fact that the remaining process steps (the regeneration subsystem) are decoupled from the gas-cleaning subsystem. This decoupling is done by providing adequate storage or surge capacity for both dry product and regenerated scrubbing solution.

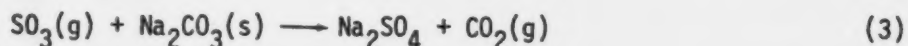
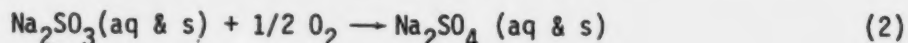
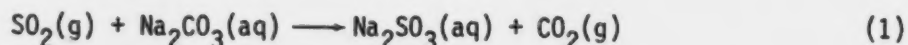


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Figure 1. ACP Block Diagram

Gas-Cleaning Subsystem

The flow diagram for this subsystem is shown in Figure 2. The flue gas enters the gas-cleaning subsystem after leaving an existing electrostatic precipitator. If no precipitator is available, a bank of cyclones would be provided, to lower the flue gas fly ash content to 1.0 grains/scf or less before it enters the subsystem. The flue gas enters the spray dryer scrubber at the top, and passes downward through a spray of fine droplets of sodium carbonate solution. These droplets are generated by a centrifugal atomizer, which drives the droplets radially outward, in crossflow to the flue gas. The following reactions take place:



Reaction 1 accounts for most of the SO_2 removal; the aqueous sulfite formed is subsequently dried to solid sulfite powder. Reaction 2 accounts for most of the sodium sulfate formed. Reaction 3 also produces sulfate and removes SO_3 ; it occurs in the cyclones and electrostatic precipitator as well as in the scrubber. The dry product formed by these reactions and collected for regeneration is usually about 60% sulfite, 20% sulfate, and 20% unreacted carbonate.

Typical liquid-to-gas (L/G) ratios for the spray dryer scrubber are 0.3 gal/1000 scf of gas. Because of this low L/G, there is not enough water injected into the spray dryer to saturate the flue gas. Therefore, its exit temperature is in the 150 to 200°F range, and the spent reactant is entrained as dry particles. The bulk of these particles are removed in the product collection cyclones, and most of the remainder are removed in the precipitator. Particle emissions to the stack will be 0.01 grains/scf or less.

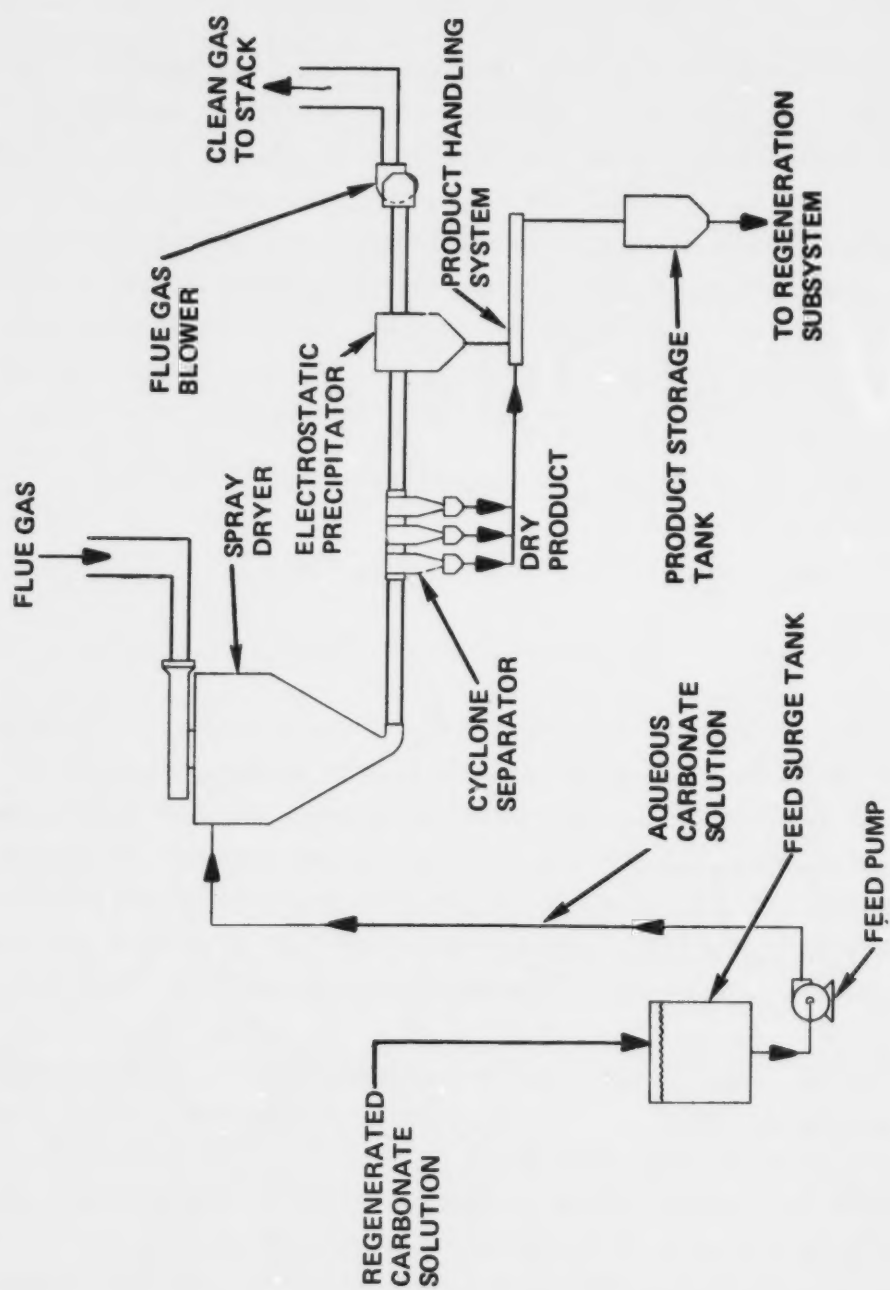


Figure 2. Gas Cleaning Subsystem Process Flow Diagram

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The key to the operation of the spray dryer scrubber is the atomization of the carbonate solution. High-speed centrifugal atomizers are used to achieve the desired spray distribution. These atomizers are capable of producing fine droplets from either solutions or slurries, at minimal liquid pumping pressure. The energy required for atomization is supplied by a spinning disc, and not by a nozzle constriction.

A desirable feature inherent in centrifugal atomization is the simple turndown method. As gas flow decreases, the solution flow rate is decreased in direct proportion. Under turndown conditions, any contact inefficiency caused by a lower gas velocity in the scrubber is compensated for by the increased atomization efficiency of the disc at the lower liquid flow rates. Excellent SO_2 removal efficiency has been demonstrated at turndown ratios of 4 to 1 for a single scrubber, and large installations requiring two or more scrubbers could readily achieve an 8 to 1 or better turndown without sacrificing pollution control capability.

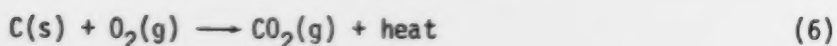
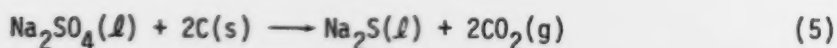
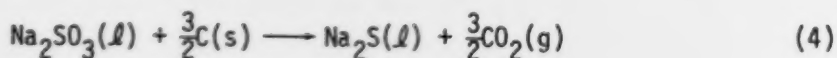
Turndown of the product collection equipment is also straightforward. For single scrubber systems, isolation dampers are provided on each bank of 8 cyclones to maintain the optimum gas velocity and collection efficiency at reduced gas flow. Also, as gas flow decreases, the precipitator collection efficiency increases because of the longer gas residence time in it. The turndown ratio of the product collection equipment is therefore compatible with that of the spray dryer, and particulate emissions of <0.01 grain/scf can be maintained under all operating conditions.

The gas-cleaning subsystem also possesses excellent pollution control capability for other acidic gases, such as HCl , SO_3 , etc. In particular, the presence of an electrostatic precipitator virtually eliminates an SO_3 plume problem.

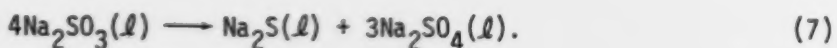
Regeneration Subsystem

Reduction. The dry product collected in the gas cleaning subsystem is stored in a silo or hopper, from which it is conveyed pneumatically to the reducer. The reducer is a refractory-lined steel vessel, which contains a pool of molten sodium carbonate and sodium sulfide.

The feed material (a mixture of dry scrubber product and carbon) is blown into the molten salt pool with air, and additional air is injected to react with a part of the carbon reducing agent. (This agent can be petroleum coke or the same coal used in the power plant.) The temperature of the reducer melt pool is maintained in the 1700 to 1900°F range; the dry feed material melts and mixes with the salt pool, and the carbon reacts with the sulfite and sulfate, reducing both to sodium sulfide. The following reactions take place:



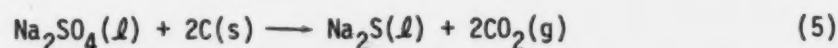
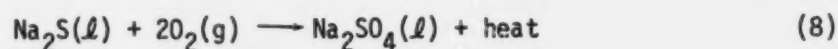
Reaction 4 is the reduction of sulfite; it probably also occurs to a large extent through a disproportionation step, since sulfite is unstable at the reducer temperature:



This disproportionation is followed by the reduction of sulfate according to Reaction 5.

Reactions 4 and 5 are endothermic, requiring heat input, and additional heat is required to heat up all of the feed material and to melt

the salt feed, as well as to compensate for heat losses through the vessel walls and heat carried out with the melt product stream and the off-gas. The heat is generated by the oxidation of a part of the carbon, as is shown simplistically in Reaction 6. Actually, much of the heat is generated by the reoxidation of sodium sulfide, which is in turn re-reduced by the carbon. The mechanism for this is



The sum of these two reactions is Reaction 6.

The reducer vessel is a vertical cylindrical steel shell with a lining of high-density, fuse-cast, alpha-alumina bricks (Monofrax A, from the Carborundum Corp.). This material has been found to be very durable in the reducer environment; indeed, corrosion rates are less than 0.5 mil/yr. The reducer is provided with an air compressor for air-feed injection, spent-reactant and carbon feed systems, off-gas conditioning equipment, startup preheaters, and a continuous melt drain spout.

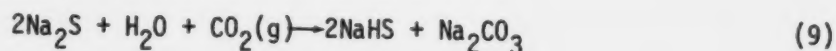
Less than 5% excess carbon (over the reduction and heat generation requirements) is used to insure 95% reduction of the sulfur-containing salts. Air is injected in sufficient quantity to oxidize the amount of carbon required for heat generation. The typical reducer off-gas contains less than 1 vol % of oxygen and up to 35 vol % carbon oxides, with CO_2/CO ratios of 10 to 1 or greater. Heat is recovered and steam is generated in a waste heat boiler prior to cooling the reducer off-gas for use in the carbonation step.

The most volatile salt in the reducer melt is NaCl, which will be the predominant particulate in the reducer off-gas. A gas cooling tower for the reducer off-gas will remove the NaCl-rich particulates and a part of the recirculating cooling tower liquid stream will serve as the chloride purge for the ACP system.

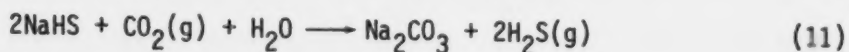
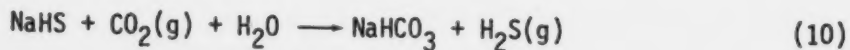
Extensive pilot-scale tests of the reduction step have been conducted in the AI Molten Salt Test Facility (MSTF). This facility and the tests are described later in this paper.

Quenching and Filtration. The quenching and filtration steps have both been demonstrated in AI bench- and pilot-scale tests, and both are employed in the pulp and paper industry in conjunction with recovery boiler operation. Recent work has also shown that the quench step can be eliminated by cooling the reduced melt, allowing it to solidify, and then breaking it up into chunks for dissolution. The solidified melt is quite porous, and readily soluble.

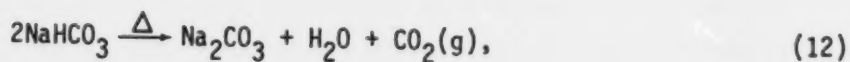
Carbonation. After dissolution and filtration, the clarified solution (green liquor) is contacted with the carbon-dioxide-rich reducer off-gas to regenerate sodium carbonate and evolve hydrogen sulfide. The green liquor is first treated in a precarbonator to form sodium hydrosulfide (NaHS), by Reaction 9.



The precarbonated liquor is further reacted with CO_2 in the carbonator, and the following reactions occur:



The Claus plant feed gas is taken directly from the carbonator. The bicarbonate slurry produced in the carbonator is subsequently decomposed by the reaction:



and the CO_2 is recovered for recycle to the inlet of the carbonator.

Sulfur Production. The hydrogen sulfide concentration produced by the carbonation process is sufficiently high to allow economical conversion to elemental sulfur in a conventional Claus plant. Claus technology is considered commercially available, and therefore has not been tested as a part of the ACP development program.

STATUS OF PROCESS DEVELOPMENT

Scrubber Development

Two pilot-scale installations have been used to test and develop the spray dryer scrubber concept. The first of these installations consisted of a 5-ft diameter spray dryer and matching cyclone, plus auxiliary equipment. This unit was purchased, modified, and refurbished for installation at the coal-fired Mohave Station of Southern California Edison. The performance of the spray dryer as a scrubber was then tested using actual flue gas from the Mohave Station.

The second pilot plant scale test installation consisted of the 7-ft diameter spray dryer and associated product collection equipment that is permanently installed at a field laboratory owned and operated by Bowen Engineering, Inc., a leading U.S. manufacturer of spray drying equipment. This pilot-scale dryer is the basic tool that Bowen uses for design information to scale up each special spray dryer application. Based on data obtained here, Bowen has designed and built spray dryers up to 44 ft in diameter.

Mohave Tests (5 ft Dryer). The spray dryer system was installed at the Mohave Station in less than two weeks, and operated on a one-shift-per-day basis over a period of seven weeks (in May and June 1972) with no significant maintenance or operational problems. During the seven-week test period, about 100 tests were conducted to completely characterize the performance of the spray dryer. Since steady state can be achieved with this kind of scrubbing system in less than 1/2 hour,

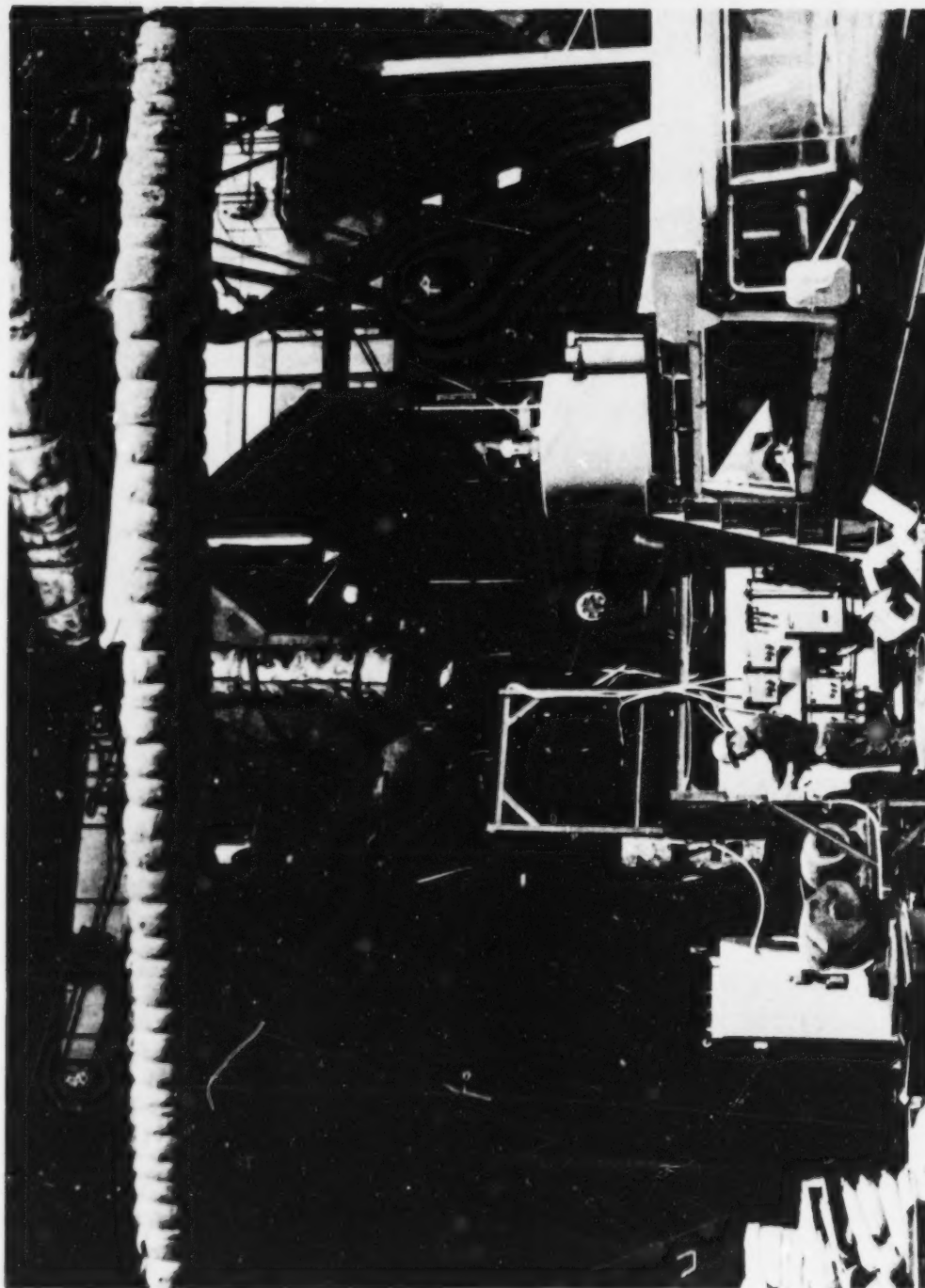
the duration of each test was typically limited to two to four hours. This allowed ample time to obtain all the required data from each test.

A photograph of the Mohave system is shown in Figure 3. In addition to the fully instrumented and controlled spray dryer system, the installation included a 560 gal. feed tank; a calibrated metering pump; duct heaters to allow variation and control of the inlet flue gas temperature; continuous monitoring instrumentation for SO_2 , NO_x , and O_2 ; and particulate sampling apparatus for product characterization. Gas flow rates were measured with an in-line flow meter, and tests were conducted at flue gas flow rates of from 1035 to 1375 scfm.

The main objective of the Mohave test program was to demonstrate 90% SO_2 removal from a flue gas containing 400 ppm SO_2 . This was accomplished by atomizing ~0.3 gal/1000 scf of a 4 to 5 wt% sodium carbonate solution into the flue gas with the centrifugal atomizer. Equally effective SO_2 removal was also demonstrated at SO_2 concentrations of up to 1500 ppm by maintaining the L/G constant at the 0.3 value and increasing the carbonate concentration. A typical plot of Mohave test results illustrating the SO_2 removal efficiency as a function of liquid absorbent feed rate is given in Figure 4.

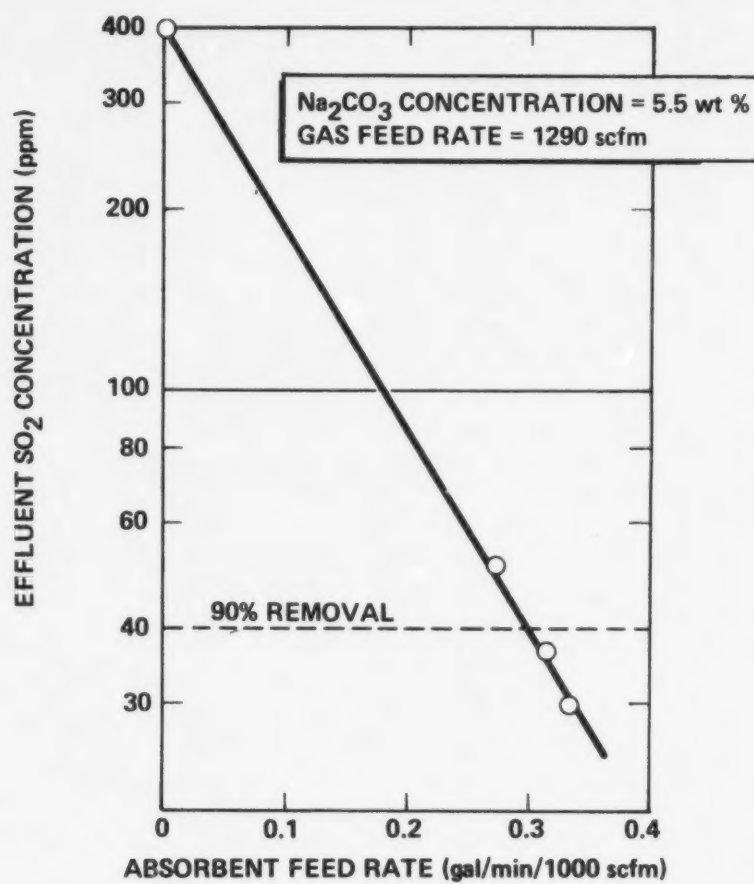
Extensive data were also obtained at Mohave relative to the collection efficiency of the cyclone. Collection efficiency ranged from 86 to 99.5% depending on the test conditions, varying primarily as a function of the particulate loading in the gas.

The Mohave installation was shut down in mid-June 1972 while the data from the test program were analyzed and the report prepared. It was reactivated in September 1972, for the purpose of additional testing with inexpensive crude soda ash. Ten tests were conducted using a trona salt obtained by surface mining of deposits at Searles Lake, California. The results generally confirmed that any soluble sodium-based alkaline material could be used for effective SO_2 removal in a spray dryer.



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Figure 3. AI Scrubber Test Installation



72-025-52-18

Figure 4. SO₂ Removal
vs Reactant Flow Rate

Bowen Tests (7 ft Dryer). A series of 26 tests was conducted in May 1973 to expand the SO_2 concentration data base and to demonstrate the turndown capabilities of the spray dryer scrubber. Tests were run at SO_2 concentrations from 175 ppm to 2120 ppm SO_2 and with gas flow rates from 1000 to 4000 scfm. The Mohave test conditions were duplicated in some of the tests, to verify that the data obtained were equivalent to those obtained when using real flue gas. The results from these tests were virtually identical to the corresponding Mohave results.

Another important result related to the gas flow capacity of the spray dryer and the turn-down characteristics. It was found that excellent SO_2 removal efficiency could be maintained by adjusting the solution feed rate in direct proportion to the gas flow rate. With all other conditions except solution feed rate held constant, gas flow rates were varied from 1000 to 4000 scfm. The SO_2 removal efficiency of the spray dryer remained at 90% or better over this entire range. In fact, SO_2 removal tended to increase slightly at the higher flow rates.

The rated capacity of the seven foot dryer is ~3000 scfm. Since the performance was excellent at 4000 scfm, 30% above the rated capacity, it is postulated that large-scale spray dryers for ACP applications can be designed to handle a greater gas flow than is typical for other spray dryer applications. This must be verified, however, in a full-scale test. The first large-scale ACP system will be designed according to standard spray dryer practice, but tested at gas flows greater than its rated capacity.

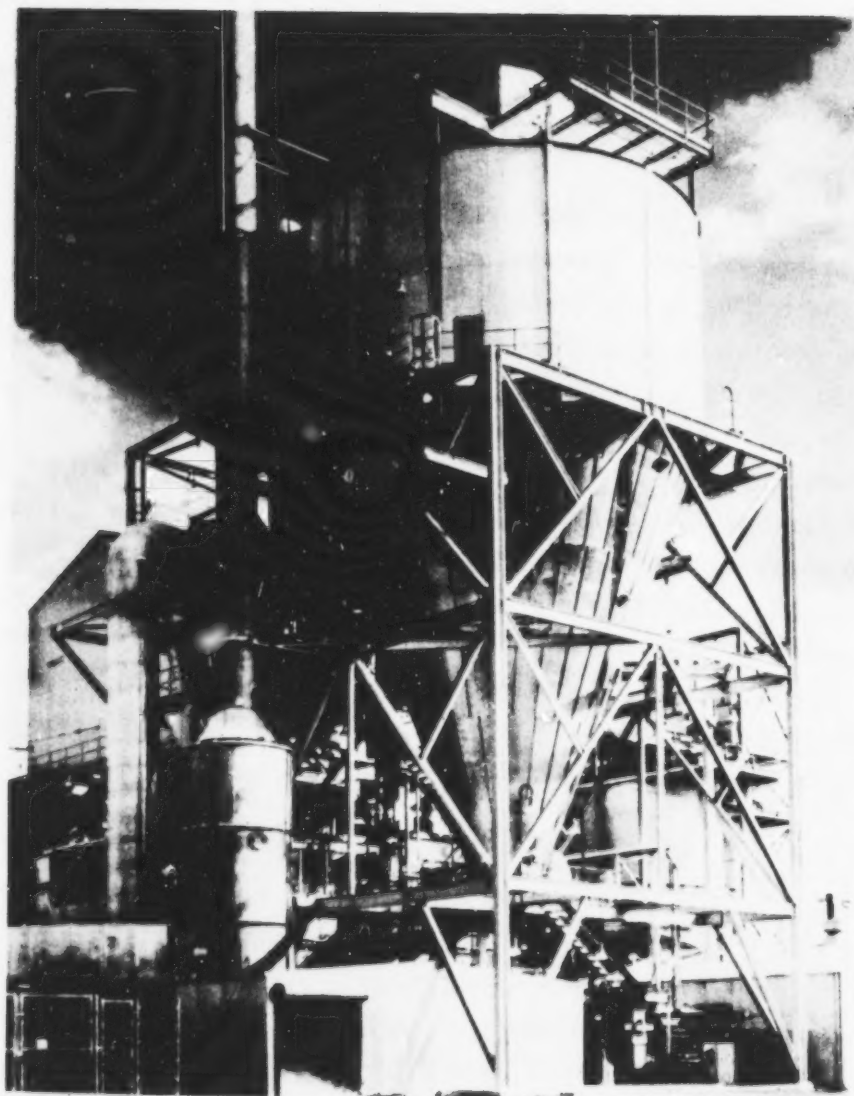
A series of 40 additional tests was conducted at the Bowen facility in June 1973, to further expand the data base by extending the SO_2 concentration range to 7200 ppm. Test results in the 200 to 3000 ppm range were in agreement with data and extrapolations from previous Bowen and Mohave tests. Tests run with SO_2 concentrations of 4000 to 7200 ppm required inlet gas temperatures of 400 to 500°F in order to insure the production and collection of a dry product; SO_2 removal efficiencies of from 92 to 99% were achieved.

The 7200 ppm SO_2 was the maximum concentration that could be generated with the available SO_2 injection apparatus. Without this limitation, the spray dryer could have been operated at higher inlet gas temperatures and with correspondingly increased SO_2 concentrations. An estimate of the dryer's performance, with its nominal maximum inlet temperature of 1200°F , indicates that about 95% SO_2 removal would be obtained with an SO_2 concentration of at least 20,000 ppm.

Large-scale spray dryers for the ACP system will utilize multiple atomizers in a single drying chamber. Bowen Engineering recently modified their pilot dryer to accommodate three centrifugal atomizers. Tests were run in October 1975 to demonstrate the feasibility of the multiple atomizer concept. About 1/3 of the incoming gas was distributed to the vane ring above each atomizer. In the first series of tests, about 1/3 of the total Na_2CO_3 solution was also fed to each atomizer. As expected, SO_2 removal efficiency was comparable to that previously obtained with a single atomizer.

A subsequent series of tests was run with one of the atomizers shut off, but with gas still flowing through its vane ring. Using the same total Na_2CO_3 solution as in the first series, but feeding 1/2 of the solution to each of the two operating atomizers, SO_2 removal efficiency remained the same as that observed in the first tests. Thus, the multiple atomizer concept was not only found to be feasible, but its use will apparently enhance operational reliability of the ACP gas cleaning subsystem.

Summary. Pilot tests of the ACP spray dryer scrubber and its associated cyclone collector have been run with gas flow rates up to 4000 scfm. One of the pilot installations is the standard scale-up tool used by the spray dryer manufacturer for the design of large-scale (up to 44 ft diameter) equipment. In fact, although the application is somewhat different, full-scale spray dryers of the size needed in a 100 Mw ACP system are currently in operation (see Figure 5).



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Figure 5. Large-Scale Spray Dryer
Installation

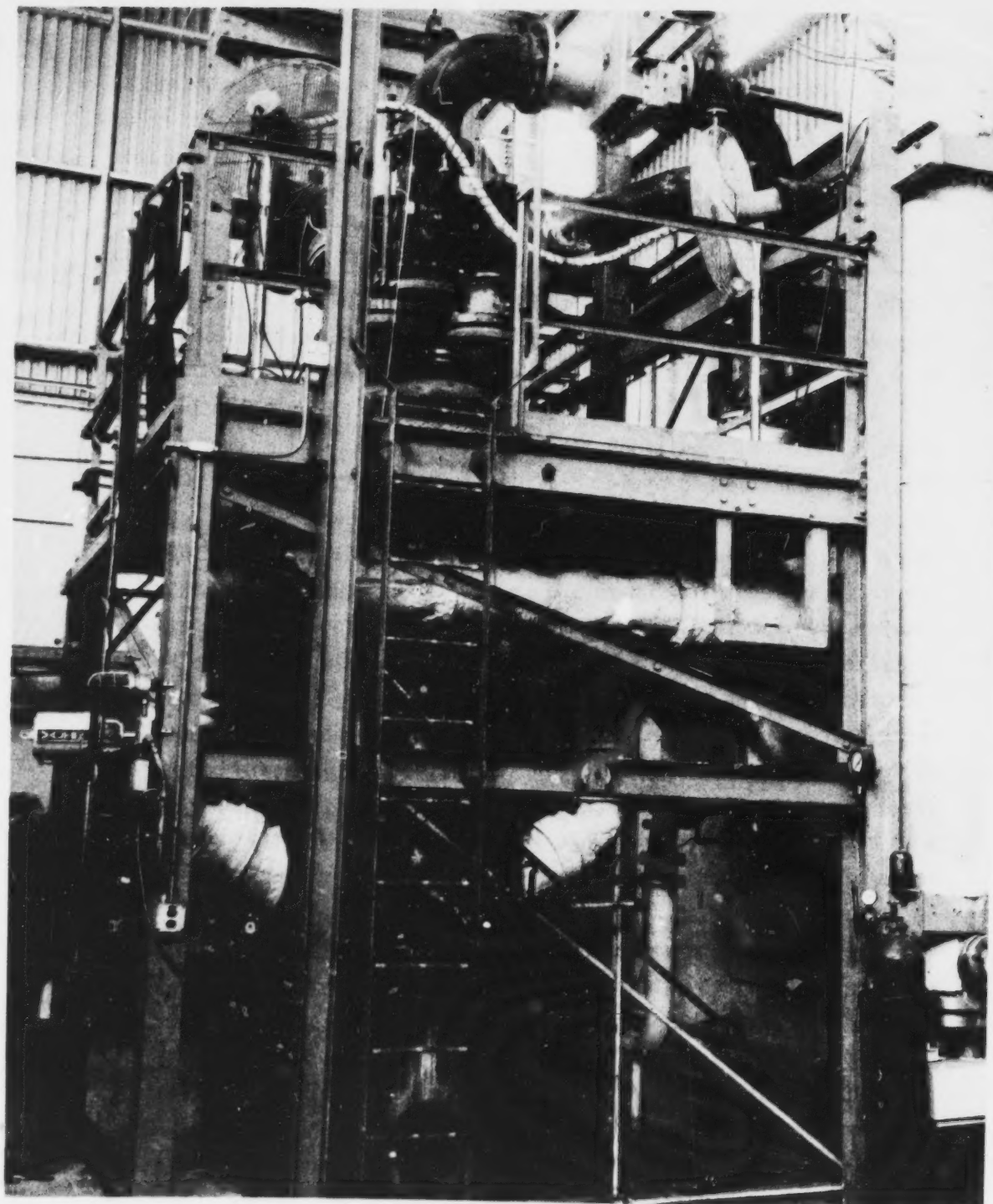
Reducer Development

The development of the ACP reduction step has proceeded from bench-scale tests in a 6 in. diameter alumina vessel to full pilot-scale testing in the Molten Salt Test Facility (MSTF) built by Atomics International for a variety of molten salt development work.

Bench-Scale Tests. The first bench-scale tests of the basic ACP reduction concept were conducted early in 1973, using small electrically-heated reactor vessels. The objectives of the tests were to establish reaction conditions, determine offgas characteristics, and obtain kinetic data.

A second bench-scale test series was conducted in early 1974 to demonstrate the feasibility of simultaneous heat generation and reduction in the ACP reducer. Solids were fed to the reducer at a rate of ~70 gm/min; 2 to 3 scfm of air was continuously injected; and the offgas was sampled for CO_2 , CO, and O_2 . The CO_2/CO ratio was measured to be >10 to 1 under optimum conditions. Residual carbon in the melt was kept at the 0.6 to 2.5 wt% level, and steady-state reduction of between 85 and 90% was achieved.

Pilot Scale Tests. Three series of pilot scale ACP reducer tests have been conducted in the AI Molten Salt Test Facility (MSTF). A photograph of this facility is shown in Figure 6. The refractory-lined vessel is three feet ID and 12 feet high. Solids and combustion air are fed into the reaction zone below the melt level through a side-entering port. The major limitation of the MSTF is its batch-type operation, but recent modifications will allow future tests to be performed with continuous withdrawal of melt product. Its capacity is sufficient to obtain steady-state data at feed rates up to 300 lb/hr (100 lb/hr equivalent to ~1 Mw) in batch-type operation, and at feed rates of 500 lbs/hr using the new continuous withdrawal capability.



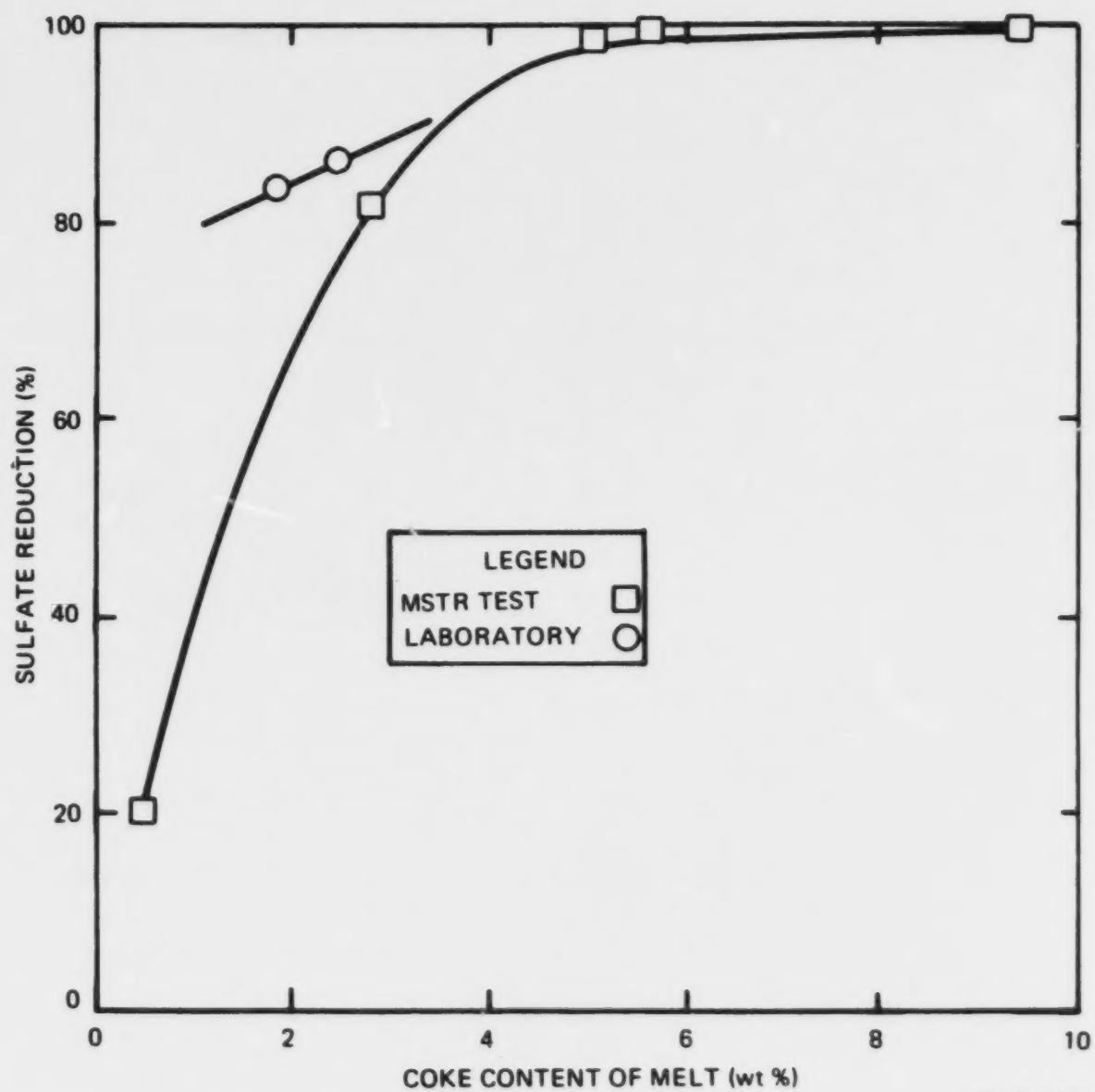
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Figure 6. Molten Salt Test Facility

The first series of tests was conducted in the MSTF to verify bench-scale results and provide preliminary design data for equipment studies. About 1670 lb of salt containing 30 wt% Na_2CO_3 , 26 wt% Na_2SO_4 , and 44 wt% Na_2SO_3 was fed at a rate of 125 lb/hr. The extent of reduction was found to be a function of the excess coke present in the melt. As shown in Figure 7, at least 90% reduction was achieved with about 3.5 wt % excess coke. This reduction rate is consistent with the bench-scale data, which are also plotted for comparison. Approximate CO_2/CO ratios of 9 to 1 or greater were observed under the test conditions. This result is again consistent with the bench-scale results.

A second series of ACP reducer tests was conducted to optimize reducer operating conditions at the pilot plant scale, improve the gas analysis techniques to obtain continuous off-gas monitoring of CO_2 and CO , and obtain data relevant to the design of larger-scale reducers. About 2300 lb of spent ACP reactant salts were fed to the MSTF during the tests at feed rates up to 150 lb/hr. Temperature was maintained between 1800 and 1850°F during the tests by reacting coke with air to generate heat. Because of the high relative heat losses in the MSTF as compared to larger vessels, and the correspondingly high air requirements, carbon oxide concentrations in the off-gas were only about 25 vol % as compared to the 35 vol % expected in full-scale reducers. The measured CO_2/CO ratios were excellent, with 80 to 1 observed during some of the tests. A more typical CO_2/CO ratio for the tests was in the range of 10 to 15 to 1, well above ACP design requirements.

Twenty melt samples were taken during the test period, and analytical results showed steady-state reduction of 90 to 95%. This again meets or exceeds ACP system design requirements. Within the constraints of the MSTF itself, the test conclusively demonstrated the feasibility of the basic ACP reduction concept, and provided satisfactory design and operating data for scale-up purposes. The MSTF lining material, Monofrax A, has been observed to be very resistant to corrosion by the melt. Corroborating test data show corrosion rates of <0.1 mil/year at 900°C (1650°F), and <0.5 mil/year at 1000°C (1830°F).



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Figure 7. Sulfate Reduction
vs Coke Content of the Melt

A third ACP reducer test series was run using a low-sulfur, high-ash, western coal as the reducing agent. Nearly 3000 lbs of salt and about 1800 lbs of coal were fed to the MSTF during the test program. Average feed rates during steady-state operation were 370 lbs/hr of salt and 180 lbs/hr of coal. The steady-state reduction rate was 89%, and the off-gas composition was found to be suitable for subsequent use as a carbonating gas. This test series provided the same type of data for coal as the second reducer test series provided for coke. A final test series is currently in the planning stages. It will utilize a high-sulfur eastern coal as the reductant, and it will also demonstrate the new continuous withdrawal capability of the MSTF.

Summary. The essential elements of the basic ACP reducer have been pilot tested. Design information from the MSTF tests has been incorporated into a preliminary reducer design study, and control diagrams for ACP reducer operation have also been prepared. Reducer design studies are continuing, and a preliminary specification for the ACP reducer-quench subsystem is in preparation.

Quenching and Filtration Development

Early in the ACP development program, laboratory tests were run to establish the filtering characteristics of coal ash suspended in solutions of sodium carbonate and sodium sulfide. The most important result established by the tests was that sodium values could be recovered from the ash filter cake with a simple washing technique. The original cake contained sodium equivalent to 20% of that remaining in the filtrate. Two wash cycles reduced that sodium level to less than 1.0% of the cake weight. More recently, a rotary drum vacuum filter was used to test the filtration of coal ash from green liquor prepared from the melt produced in the third reducer test series.

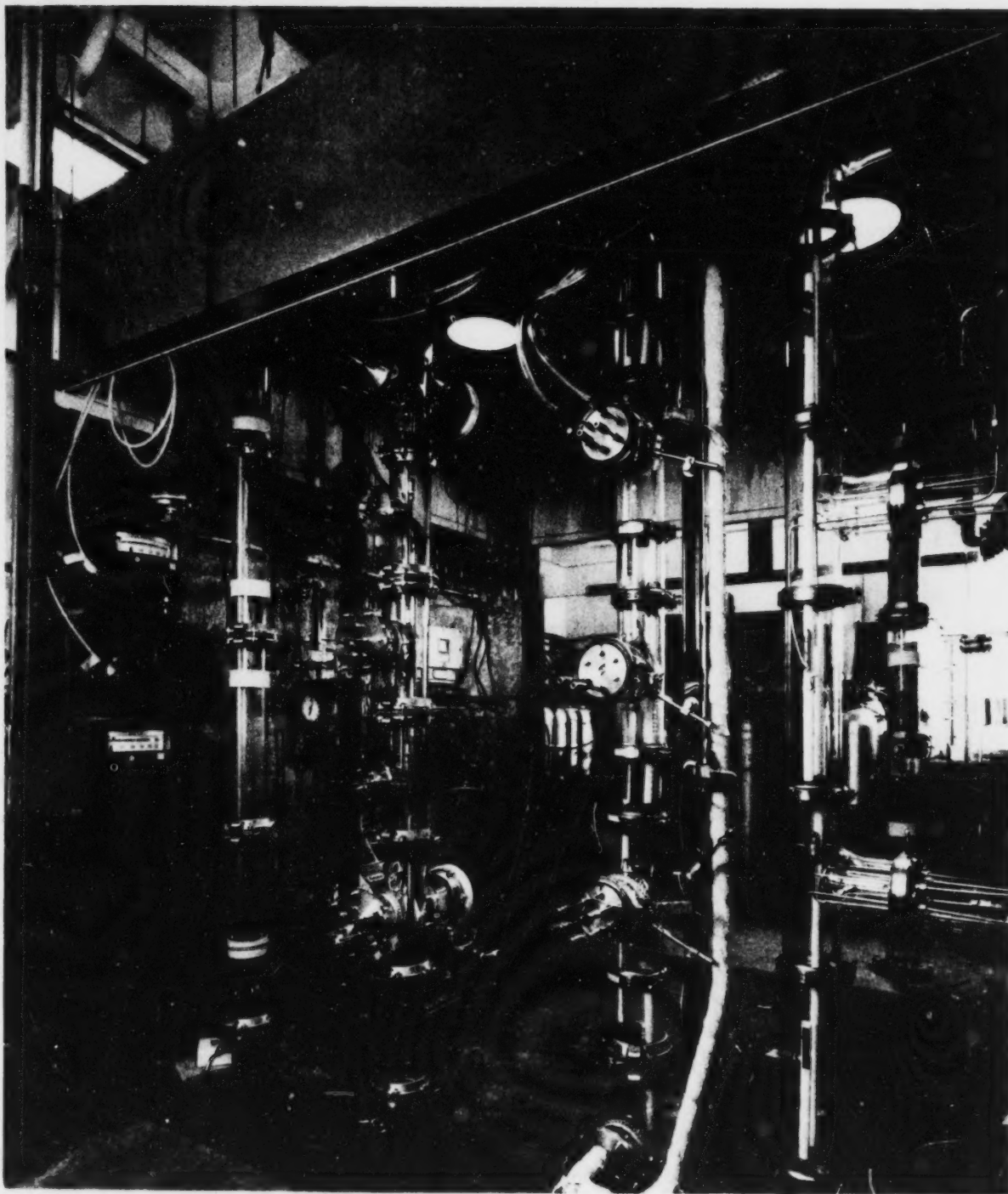
Quenching tests were conducted in AI laboratories during 1974 to provide basic chemical and physical information. Up to 20 lb/min of a 70% sodium sulfide - 30% sodium carbonate melt were quenched and dissolved in a 14 cu ft tank. The key to trouble-free quenching was found to be adequate dispersion of the melt into fine droplets, and maintaining the bulk dissolving liquor at or near its boiling point.

Carbonation Development

The development of the ACP carbonation step originated with an extensive literature survey and analysis of existing carbonation technology used in the chemical and pulp industries. The essential conclusion of this study was that AI should embark on a development program specifically aimed at devising a carbonation scheme to take advantage of the key ACP features.

Accordingly, a small pilot-scale development program was initiated. The pilot unit was designed, built, and tested during the past two years. A photograph of the equipment is shown in Figure 8. It consists of a series of glass columns with stainless steel internal hardware. A gas supply system, a small steam generator, and appropriate pumps and valves complete the equipment array for the pilot unit. An engineering support effort was initiated in parallel with the development program to make the work relevant to the design constraints of a large-scale system. As a result of this cooperative effort, the original carbonation scheme was modified, and is now considered to be the best alternative for this ACP process step.

Extensive tests (>100) were run to evaluate the parameters affecting the carbonation sequence. The data obtained included parametric and steady-state characterization of performance in terms of the gas-liquid reactions, temperature effects, and column configurations. One of the key design requirements of the carbonation step is the efficiency of H_2S stripping in the carbtorator. The reference design value derived in



4137-6

Figure 8. Carbonation Pilot Plant

engineering studies was 98.6%. Pilot test results were typically above 99%, and were above 99.9% in many cases.

The most recent tests of this process step utilized the clarified green liquor that had been generated by sequentially processing the melt from the third reducer test. Over 200 gallons of clarified green liquor were carbonated. This test was of major importance because it closed the process loop, and it clearly established that the use of coal will not significantly affect the basic ACP process steps.

Commercial Components

The two major components of the ACP system which have not been tested are the electrostatic precipitator and the Claus plant. These components are commercially available without specific testing for the ACP application.

Electrostatic Precipitator. Electrostatic precipitators are used as the final particulate collectors in the basic ACP system. Specifications have been written and quotes and guarantees obtained for this component.

Claus Plant. Commercially available Claus plants will be used to produce elemental sulfur in the ACP system. The AI-developed carbonation step produces 35 vol% H_2S gas, a suitable feed for the Claus reaction.

PROJECTED PROCESS ECONOMICS

The capital investment requirements and total annual operating costs for an ACP system installed on a new 500 Mw, coal-fired power plant have been estimated, in a preliminary economic evaluation performed by Atomics International with the help of the Stack Gas Emission Studies Staff of TVA. The basis for the estimates were the same as those used by TVA in a recent EPA-sponsored study of other advanced flue gas desulfurization processes.⁽¹⁾ The costs are for a plant with a mid-1975 startup.

The total capital investment for the 500 Mw ACP system was estimated at \$32,067,000. This compares favorably with another sulfur-producing process evaluated by TVA. The net total annual operating costs for the 500 Mw ACP system were estimated at \$7,783,200. This compares favorably with the limestone throwaway process, which had the lowest operating costs of all the processes evaluated by TVA. Based on this economic evaluation, which provided a unique opportunity to compare the ACP system with other advanced flue gas desulfurization processes on the same basis, the ACP system is among the best of the regenerative processes currently being developed.

Capital Investment Summary

A summary of the estimate for the capital costs of the 500 Mw ACP system is given in Table 1. The total direct investment is \$19,835,000, and the total capital investment is \$32,067,000 or \$64/kw.

The indirect costs for engineering, construction, and contingency were taken as percentages of direct investment, and they are self-explanatory. They total 37% of the direct investment and are, therefore, a very substantial part of the total investment. The other indirect costs for startup and interest during construction were taken as 10% and 8% of the fixed investment. They are also substantial.

Operating Costs

A summary of the estimate for the total annual operating costs of the 500 Mw ACP system is given in Table 2. The direct costs are estimated at \$3,063,000/year. Indirect operating costs, including 14.9% of the total capital investment, are estimated at \$5,672,000/year. The gross total annual operating costs are \$8,736,100/year or 2.5 mills/kwh for the assumed 7000 hr/yr load factor. This total does not include a credit for the sulfur produced, although a marketing expense to sell the sulfur was charged under indirect operating costs.

TABLE 1
TOTAL CAPITAL INVESTMENT REQUIREMENTS
500 Mw System
(Mid-1974 Equipment Delivery)

<u>DIRECT COSTS</u>	<u>TOTAL</u>
• EQUIPMENT	13,392
• PIPING AND INSULATION	636
• DUCTWORK, CHUTES, AND SUPPORTS	1,628
• CONCRETE FOUNDATIONS	278
• EXCAVATION, SITE PREPARATION, RAILROADS, ROADS, AND POND	331
• STRUCTURAL	233
• ELECTRICAL	1,293
• INSTRUMENTS	724
• PAINT AND MISCELLANEOUS	113
• BUILDINGS	244
• LAND	18
• CONSTRUCTION FACILITIES	945
■ SUBTOTAL DIRECT INVESTMENT	19,835
<u>INDIRECT COSTS</u>	
• ENGINEERING DESIGN AND SUPERVISION	2,182
• CONSTRUCTION FIELD EXPENSE	2,182
• CONTRACTOR FEES	992
• CONTINGENCY	1,984
■ SUBTOTAL FIXED INVESTMENT	27,175
• ALLOWANCE FOR STARTUP AND MODIFICATIONS	2,718
• INTEREST DURING CONSTRUCTION	2,174
■ TOTAL CAPITAL INVESTMENT	32,067

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TABLE 2
TOTAL ANNUAL OPERATING COSTS
500 Mw System
(Mid-1975 Startup)

	UNIT COST (\$)	TOTAL ANNUAL QUANTITIES	TOTAL ANNUAL COST (\$)
<u>ANNUAL DIRECT COSTS</u>			
• DELIVERED RAW MATERIALS			
■ SODA ASH (tons)	52/ton	420	21,840
■ COKE (tons)	15/ton	45,500	682,500
■ CATALYST			24,000
	▲ SUBTOTAL RAW MATERIALS		728,340
• CONVERSION COSTS			
■ OPERATION LABOR & SUPERVISION	8.00/ man-hr	39,840	318,720
■ UTILITIES			
▲ FUEL OIL (NO. 6), (gal)	0.23/gal	1,470,000	318,100
▲ COOLING WATER (Mgal)	0.02/Mgal	1,822,000	36,440
▲ PROCESS WATER (Mgal)	0.08/Mgal	145,740	11,670
▲ TREATED WATER (Mgal)	0.30/Mgal	24,780	7,430
▲ ELECTRICITY, (kwh)	0.01/kwh	74,492,000	744,920
▲ MAINTENANCE (LABOR & MATERIAL)			758,500
▲ ANALYSES	12.00/hr	9,960	119,520
	▲ SUBTOTAL CONVERSION COSTS (\$)		2,335,300
	▲ SUBTOTAL DIRECT COSTS (\$)		3,063,600
<u>INDIRECT COSTS</u>			
• AVERAGE CAPITAL CHARGE AT 14.9% OF INVESTMENT			4,778,000
• OVERHEAD			
■ PLANT, 20% OF CONVERSION COSTS			467,100
■ ADMIN & MARKETING COSTS			427,400
	▲ SUBTOTAL INDIRECT COSTS (\$)		5,672,500
	▲ TOTAL ANNUAL OPERATING COST (\$)		8,736,100

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The direct operating costs include raw materials, operating labor and supervision, utilities, maintenance, and analytical support labor. Maintenance requirements for the ACP system were estimated as percentages of direct investment for the various process areas. The three ACP areas which are somewhat unique are particulate scrubbing, SO₂ scrubbing, and reduction. Since the ACP particulate scrubbing area consists of only cyclones and ducts, maintenance requirements should be very low. The ACP SO₂ scrubbing area should also be low, with the electrostatic precipitators requiring the highest degree of maintenance. These two maintenance factors were specifically checked by TVA against their own power plant operating data and found to be valid. The major maintenance user in the ACP system is reduction, which was assumed to require an 8% factor. This factor is the maximum assessed against any regeneration area for the processes studied by TVA.

The capital charge used by TVA is 14.9% of total capital investment. For the ACP system, with an investment of \$32,067,000, this charge totals \$4,778,000 or almost 55% of the total annual operating costs. Plant overhead was assumed to be 20% of the conversion costs. Conversion costs include all direct operating costs except those for raw materials. The final indirect cost is for administrative overhead and marketing of the process byproduct. An arbitrary total figure of \$427,400 was charged for this indirect cost.

If the administrative and marketing overhead is broken down in accordance with the TVA ground rules for other processes, it includes \$31,900 for administration (10% of operating labor), and \$395,500 for product marketing. Since the ACP system and other regenerative processes incur this expense, it is only fair that a product credit be given. The ACP system produces 5.445 tons/hr of sulfur which is worth \$952,900/yr assuming a credit of \$25/ton. This was the credit used by TVA in their analyses of the long-term operating costs of flue gas desulfurization systems. Although not shown on Table 2, the net total annual operating costs for the ACP system, including the product credit, are \$7,783,200/yr or 2.2 mills/kwh.

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ENERGY REQUIREMENTS FOR SHELL FGD PROCESS

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ENERGY REQUIREMENTS FOR SHELL FGD PROCESS

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Introduction

In the normal evaluation and comparison of flue gas desulfurization systems, it is usual to make an overall economic analysis including capital as well as operating costs, and to determine annual charges for the projected operational load over the real life of the equipment. The cost estimates prepared by the engineers in the Chemical Development Division of TVA illustrate this procedure in impressive detail.⁽¹⁾ With this type of study the annual charges are often computed back to present dollars to yield a single value, characteristic for each process, as applied to a given problem and a given set of factors, i.e., utilities, catalysts, chemicals, labor, maintenance, taxes, finance procedures, interest, and capital recovery rates. This single number represents the amount of present dollars which at a preselected rate of interest would finance the entire operation from engineering and construction through the final day of the units life.

Such an analysis has the advantage of permitting a comparison on a single economic scale of complex processes of different types, e.g., regenerative vs. throwaway. The basic limitation of this technique lies in the inability of the analyst to predict the costs of utilities over the normal life span of the plant, e.g., 30 years. In contrast with capital charges which occur in the immediate future and hence which can be cost-estimated with some accuracy, the cost of fuels are often affected by unpredictable factors. However, a single predictable characteristic related to projected fuel costs is the inevitability of continuously increasing costs of all fuels.

With the major adjustments in fuel prices that have occurred in the last several years, it has become common practice to supplement the economic analysis with a survey of the energy requirements as an aid to process evaluation.

Such a study of the energy requirements for the Shell FGD process is the basis for this paper.

Process Flow

The energy requirements for the Shell FGD process (2-7) expressed as fuel, steam or electrical, refer to the capture and production of a concentrated stream of SO₂ free from

particulate matter and oxygen. Note that there is, therefore, no net change in the chemical species containing the sulfur.

For a given boiler size the energy requirements can vary substantially with the amount of sulfur processed. This condition is described in Table 1, which shows the heat rates, flue gas rates, and sulfur rates for a 150 MW boiler fueled with coal containing 0.32 and 3.89% sulfur. The processing schemes were formulated to effect 85% desulfurization on flue gas containing 350 ppm (Case I) and 3500 ppm of SO₂ (Case II).

The proposed design in Case I uses three reactors in parallel to obtain the desired sulfur removal (See Figure 1). The flue gas is processed through a copper-on-alumina acceptor. Since the quantity of sulfur removed is small, the acceptance time is long (290 min.), and one additional reactor in regeneration can support three in acceptance. Thus, the cycle for each reactor becomes:

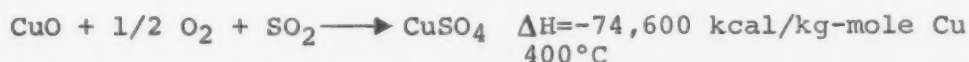
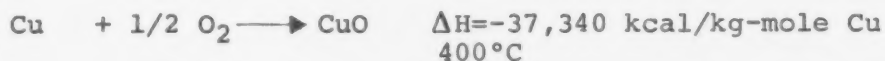
	<u>θ Minutes</u>
Acceptance	290
Valve Switch and Purge	3
Regeneration	91
Valve Switch and Purge	3
	387

Since each reactor experiences the same cycle, the average number of completed cycles per day is:

$$\text{Cycles/Day} = \frac{(1440)}{(387)} (4) = 14.9$$

Acceptance

At the start of acceptance, immediately after regeneration, purging, and valve switching, the copper in the regenerated acceptor exists as elemental copper. Upon contact with the oxygen in the flue gas, the copper reacts rapidly to form copper oxide (CuO) which in turn reacts with the oxygen and SO₂ in the flue gas to form copper sulfate (CuSO₄). The conversion of CuO to CuSO₄ is given by the net average loading (α), the fraction of the total copper present as CuSO₄. The reactions occurring during acceptance are:



The heat released during the acceptance period is (see Table 2):

$$(-37,340) + (a) (-74,600) = \frac{-85,084 \text{ kcal/kg-mole Cu}}{\text{at } 400^{\circ}\text{C}}$$

where $a = 0.64$.

This exothermic heat is absorbed by the flue gas and results in a temperature increase. In Case I, for example, with a net average loading of 0.64, the average hourly temperature raise is calculated:

Basis: 1 kg-mole Cu

$$\text{Flue gas processed, kg/basis} = \left(\frac{0.64}{0.85} \right) \left(\frac{100}{0.035} \right) (29.5) = 63,462$$

where 29.5 is the molecular weight of the flue gas. The heat release of 85,084 kcal per kg-mole of copper is absorbed into this flue gas and results in an average temperature increase of:

$$\Delta T = \left(\frac{85,084}{63,462} \right) \left(\frac{1}{0.25} \right) = 5.4^{\circ}\text{C}$$

where 0.25 is the specific heat of the flue gas. If this sensible heat is recovered in the air preheater and returned to the furnace, the heat of the oxidation and acceptance reactions represents:

$$\left(\frac{6.19}{0.64} \right) (85,084) = 0.823 \text{ MM } \frac{\text{kcal}}{\text{hr}}$$

which is equivalent to 0.24% of the input heat rate, i.e., a reduction in fuel rate of 0.24%. Note also that the sensible heat represented by $(5.4)/0.24 = 22.5^{\circ}\text{C}$ is therefore equivalent to approximately 1% on boiler efficiency or 91 Btu/Kwhr reduction in heat rate.

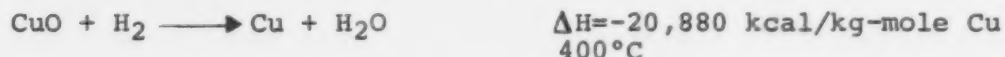
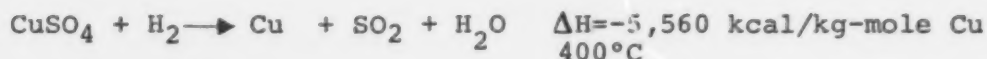
In Case II, where the amount of sulfur being processed has increased by a factor of $65.34/6.19$, the 85% desulfurization is achieved with 2 reactors in acceptance supported by one in regeneration; the loading at the end of acceptance is 0.77, the heat released per kg-mole of copper is 94,782 kcal/kg-mole, the average flue gas temperature raise is 49.6°C corresponding to 2.34% on the input heat rate to the boiler (213 Btu/Kwhr).

The heat release, resulting in an average temperature raise of approximately 49.6°C , is not uniform over the acceptance period, since the oxidation wave moves through the reactor in but a few minutes. The reactor internals are designed with sufficient heat capacity to keep peak temperatures well below that at which temperature damage to the acceptor can occur. The combined heat capacity of the SFGD reactors and the regenerative air preheater serve to smooth out the temperature

of the preheated air and cooled flue gas.

Regeneration

In the regeneration portion of the cycle the copper as CuSO_4 and as CuO is reduced to the elemental form. These reactions are:



The heat release is therefore:

Basis: 1 kg-mole Cu

$$(1-.64) (-20,880) + (0.64) (-5,560) = \\ -11,075 \text{ kcal/kg-mole Cu}$$

Since the regeneration off-gas goes to a waste heat boiler this heat of reaction is a recoverable steam credit.

It is informative to observe that the copper cycle is now completed and that each step in the cycle is exothermic, yielding up heat to the fluid being processed. Furthermore, with appropriate design of the system, this heat is recoverable as a credit against the energy requirements of the process. The reductant which "fuels" the cycle is the hydrogen used in the copper regeneration and which is rejected in a completely oxidized form, i.e., water. Note further that hydrogen is simply an intermediate product in the stepwise oxidation of fossil fuels, yielding ultimately the carbon as carbon dioxide, the hydrogen as water, and sulfur as sulfur dioxide. Thus hydrogen not only can be produced directly by the sub-stoichiometric combustion of any fossil fuel, but further, a unit of hydrogen represents a quantity of thermal energy almost independent of the fuel source, e.g., methane, light hydrocarbons, liquid residual fuels, coke, or coal. In this study, this relation between hydrogen and thermal energy is 4298 kcal/NM³. Note this thermal equivalent of hydrogen is approximately 140% of the heat of combustion.

The stoichiometric amount of hydrogen required per mole of SO_2 removed and released can be expressed in terms of the acceptor loading, a , as

$$\frac{\text{H}_2}{\text{SO}_2} = \frac{a + 1.12}{a}$$

applied to Case I, the stoichiometric hydrogen per cycle is:

$$\frac{6.19}{3} \frac{290}{60} (2.75) = 27.4 \text{ kg-mole H}_2$$

The SO₂ evolution vs. time curve appears as a block function; as long as SO₂ leaves the reactor no unreacted H₂ "slips" through. At the end of the regeneration period, when the quantity of SO₂ produced falls off sharply, H₂ appears in the regeneration off-gas.

At the end of a regeneration, the reactor void volume contains regeneration gas which is displaced during the subsequent purge through an accepting reactor where the hydrogen is catalytically oxidized by CuO to water. The heat released is absorbed by the flue gas being processed and is recoverable.

Copper sulfate at 400°C is extremely reactive with hydrogen; indeed the rate of SO₂ release can be controlled by the rate of hydrogen addition. Furthermore, there is a mole change (increase) in the copper sulfate reduction so that the course of the reaction can be easily monitored (and controlled) by observing gas flow rates to and from the reactor. An interesting characteristic of the chemistry occurs at the beginning of the regeneration when hydrogen is introduced to the purged reactor. As the first copper sulfate is reacted at the inlet of the bed, the released SO₂ is re-accepted. All the CuO is reduced before SO₂ breaks through and appears in the regeneration off-gas. The SO₂ production rate change is equally as abrupt at the end of the regeneration.

The total amount of H₂ required for one regeneration for Case I is then:

Stoichiometric H ₂	27.42 kg-mole
Slip H ₂ (10%)	2.74
Purge H ₂	1.1
	<u>31.26 kg-mole H₂</u>

This amount of H₂ must be supplied during the time allotted for regeneration (91 minutes in Case I), i.e.,

$$0.343 \frac{\text{kg-mole}}{\text{min.}}, \quad (20.6 \frac{\text{kg-mole}}{\text{hr.}})$$

In some instances the hydrogen may be available on demand, that is, supplied intermittently from a generator supplying other process units. More frequently, however, the hydrogen must be produced continuously and during the valving and purge portions of the regeneration cycle the reductant is vented to the boiler displacing its heating value equivalent as fuel.

The total hydrogen demand is converted to equivalent

fuel at the ratio mentioned above, i.e., 4298 Kcal/NM³ hydrogen. The vented and purged reductant is credited at fuel value, i.e., at its heat of combustion.

After regeneration the reactor is purged with steam at a rate of one reactor volume/minute, and like the hydrogen can be treated as an intermittent or continuous supply depending on local conditions. Frequently the steam purge requirement of one reactor volume/minute determines the supply rate. Vented steam carries no credit value.

Additional Heat Recovery

The SFGD process provides almost complete removal of SO₃. The small amount of SO₃ remaining in the processed gas is a function of the acceptor temperature and sulfur loading. In most cases the SO₃ removal results in a reduction in the sulfuric acid dew point permitting a reduction in flue gas temperature and increased thermal efficiency of the boiler. In Case I, however, the total sulfur content of the flue gas is so low, the SO₃ (normally 2-3% of the total) permits heat recovery to flue gas temperatures of 125°C. For Case II, however, SO₃ removal in the SFGD reactors permits a decrease in acid dew point of approximately 40°C.

Figure 2 gives typical SO₃ vs. dew point-temperature data from several sources. Translating to an energy credit: (See Table 2)

$$\left(\frac{492,000 \text{ NM}^3}{\text{hr}} \right) \left(\frac{0.327 \text{ kcal}}{\text{NM}^3 \cdot ^\circ\text{C}} \right) (40^\circ\text{C}) = 6.435 \times 10^6 \text{ kcal/hr}$$

Flue Gas Pressure Drop

The energy requirements discussed in the preceding development are related directly to the amount of sulfur removed from the flue gas, and have been expressed appropriately as steam or fuel debits or credits against the flue gas desulfurization. Note that these requirements can be met without derating the station being serviced. However, the electrical requirements to drive the fans and to overcome the pressure drop across the reactors, ducting and valves does represent a consumption of a portion of the station output. Fortunately, the pressure drop through the SFGD reactors is low because of the nature of the internals design wherein the gas flows through open channels. The pressure drops have been converted to electrical requirements assuming reversible adiabatic compression on a perfect gas and 75% driver efficiency.

For a hot-dry process wherein this compression work is applied upstream of the air preheater, the heat of compression is recoverable. For example, the temperature raise on the flue gas for Case I resulting from a pressure increase of 30 cm water is 5.6°C. This temperature rise is carried through the system to the preheater.

Dampen Flow

In this operation steam is generated by heat exchange with the hot regeneration off-gas and water is condensed from the released SO₂ in the quench tower. The flow of concentrated SO₂ from this system is necessarily cyclic because of the nature of the process. In the design used in this study the flow is smoothed through a gas compressor/gas holder to provide a steady feed rate to a sulfur recovery unit, e.g., Claus or sulfuric acid. The net water condensate is boiled through a small stripper; the stripped water can be used as boiler feed water directly or through the boiler feed water anion exchanger. Because the quantity is small, if desired, it may be released to the atmosphere in the flue gas.

The results of the calculations are summarized in Table 3, by case, energy class and service function. Since the units for all entries are the same, per cent on energy input to the station, the results can be summed into a single number. In Case I, with 100 units of thermal energy released in the furnace, the yield at the generator is 37.5 units of electrical energy and 0.31 of the 37.5 (0.83%) is required to drive the fans. Further, an additional 0.29 units as net fuel and steam supplies the other energy requirements to effect the desulfurization and concentration. In Case II, the net output of the station drops from 37.5 to 37.0 and total requirements increase to 3.5% on input.

SO₂ Work-up

The work-up of the concentrated SO₂ to final product, e.g., liquid SO₂, sulfuric acid or elemental sulfur, was purposely not included in the analysis since the energy requirements differ for each final product. However, it is instructive to evaluate one processing procedure on the same scale of percent of station input, e.g., a modified Claus processing SO₂ to elemental sulfur. But, now we are faced with a new concept where there is a change in chemical species of the sulfur from input to output. The fuel requirements and steam credits for a modified Claus are readily determined but note that the final form of sulfur produced is a fuel and has a fuel credit, whereas the sulfur entering the Claus as SO₂ has no real fuel value.

One manner of crediting the process for the energy value increase of product over feed is to compute the heat

release in the furnace from the oxidation to SO_2 of the sulfur in the fuel which is recovered. This has been done and the results tabulated in Table 4.

Summary

A survey of the process energy requirements as a function of the sulfur content in the fuel and based on the heat rate to the boiler, gives the development engineer a measure of the operating costs independent of external factors. The analysis presents a single number, analogous to the detailed cost estimate, which represents the operating costs of the particular process design. Such an analysis again permits the comparison, on a single scale, of complex processes.

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TABLE 1
BASIS FOR CASE STUDY

	<u>CASE I</u>	<u>CASE II</u>
MW	150	150
Heat Rate, Btu/Kwh	9100	9100
HHV, Btu/lb	8500	8500
Sulfur, Wt-%	0.32	3.89
Flue Gas Rate, SCFM	290,000	306,000
Flue Gas Rate, NM ³ /hr	466,000	492,000
SO ₂ in Flue Gas, Vol-%	0.035	0.35
Inlet Sulfur, kg-mole/hr	7.284	76.80
Desulfurization Efficiency, %	85.0	85.0
Reactors Accepting/Regenerating	3:1	2:1
Acceptance Time, Min	290.0	52.73
Regeneration Time, Min.	91	20
Valve Change & Purge, Min.	6	6
Average hourly SO ₂		
Rate Accepted, Kg-mole/hr	6.19	65.28
Net Average Loading At End		
of Acceptance Cycle, <i>a</i>	0.64	0.77
Input Heat Rate x 10 ⁻⁶ kcal/hr	343.98	343.98

TABLE 2
PROCESS UTILITY REQUIREMENTS
AS % OF STATION INPUT

	<u>CASE I</u>	<u>CASE II</u>
<u>Acceptance</u>		
Heat Release, MMKcal/hr	0.823	8.043
% of input	<u>0.24</u>	<u>2.34</u>
<u>Desorption of SO₂</u>		
Heat Release, MMKcal/hr	0.107	0.939
% of input	<u>0.03</u>	<u>0.27</u>
Total H ₂ intake, kg-mole/hr	20.6	238.5
% of input	<u>0.58</u>	<u>6.68</u>
H ₂ to vent, kg-mole/hr	1.28	54.28
% of input	<u>0.02</u>	<u>1.08</u>
H ₂ purged, kg-mole/hr	0.58	4.98
% of input	<u>0.01</u>	<u>0.10</u>
Total steam intake, kg-mole/hr	87.12	781.16
% of input	<u>0.28</u>	<u>2.50</u>
<u>Additional Heat Recovery</u>		
Temperature advantage, $\Delta T^{\circ}\text{C}$	-	40
% of input	-	<u>1.87</u>
<u>System Pressure Drop</u>		
ΔP , cm H ₂ O	30.2	39.1
Electrical requirements, Kwh/D	30241	41685
% of input	<u>0.31</u>	<u>0.43</u>
Temperature raise, $\Delta T^{\circ}\text{C}$	5.6	7.2
% of input	<u>0.25</u>	<u>0.33</u>
<u>Flow Dampening</u>		
Electrical requirements, Kwh/D	730	8500
% of input	<u>0.01</u>	<u>0.09</u>
Net Steam Produced, kg-mole/hr	7.5	71.5
% of input	<u>0.02</u>	<u>0.23</u>

TABLE 3

SUMMARY

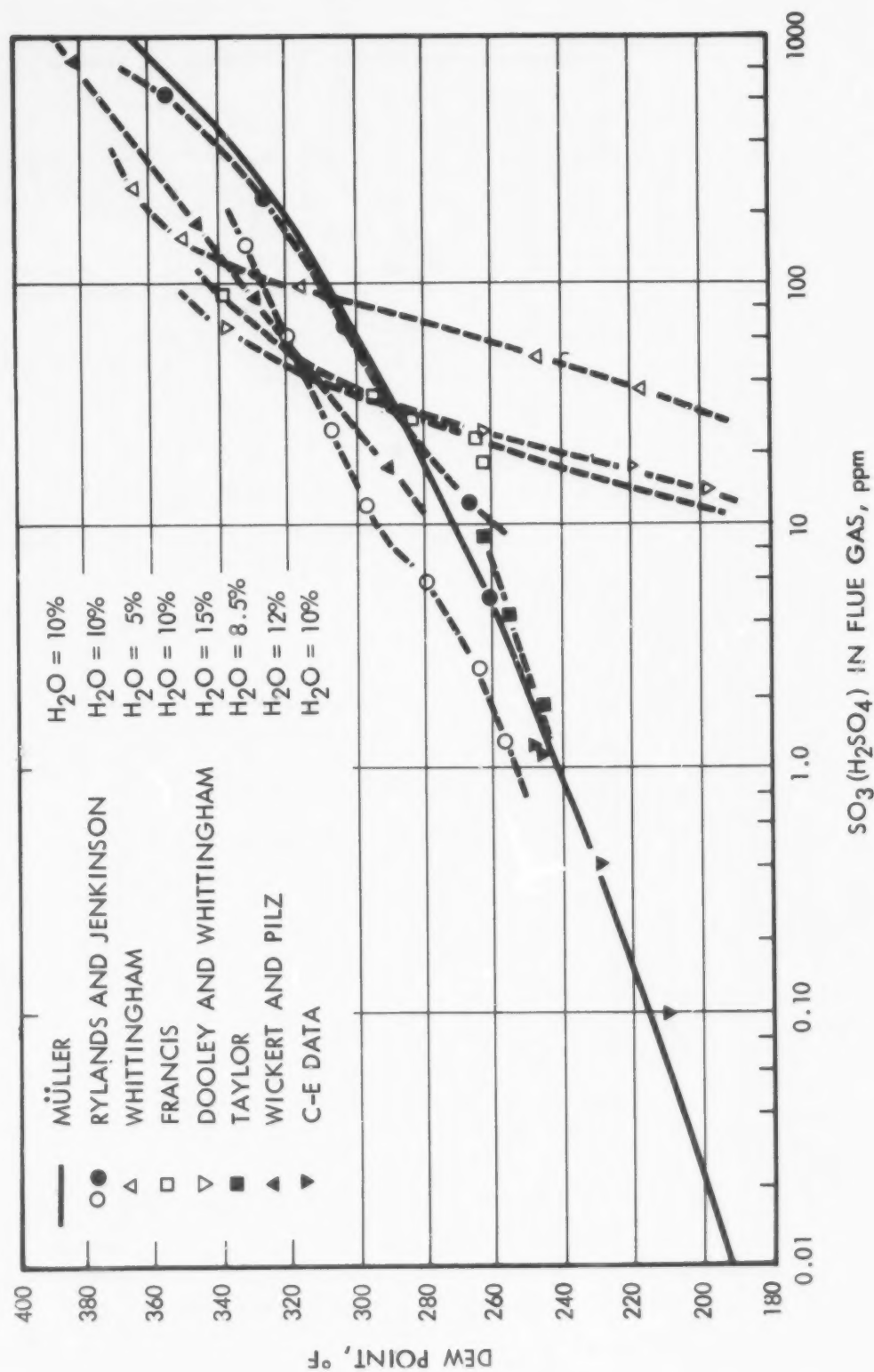
	<u>CASE I</u>			<u>CASE II</u>		
	<u>E</u>	<u>S</u>	<u>F</u>	<u>E</u>	<u>S</u>	<u>F</u>
<u>Acceptance</u>			(0.24)			(2.34)
<u>Desorb SO₂</u>		0.28	0.58		2.50	6.68
(Vent H ₂)			(0.02)			(1.08)
(Purged H ₂)			(0.01)			(0.10)
Heat Release			(0.03)			(0.27)
<u>Additional Heat Recovery</u>			--			(1.87)
<u>Pressure Drop</u>	0.31		(0.25)	0.43		(0.33)
<u>Dampen Flow</u>	0.01	(0.02)		0.09	(0.23)	
	0.32	0.26	0.03	0.52	2.27	0.69
Net energy requirement % of input			<u>0.61</u>			<u>3.48</u>

TABLE 4

SO₂ WORK-UP

	<u>CASE I</u>			<u>CASE II</u>		
	<u>E</u>	<u>S</u>	<u>F</u>	<u>E</u>	<u>S</u>	<u>F</u>
Fuel Requirements	-		0.27	-		2.85
CH ₄ credit			(0.06)			(0.53)
H ₂ credit			(0.03)			(0.32)
Steam credit		(0.09)			(0.94)	
Fuel credit for elemental sulfur produced			(0.19)			(2.24)
	-	(0.09)	(0.01)	-	(0.94)	(0.24)
Net credit overall			<u>(0.10)</u>			<u>(1.18)</u>

FIGURE 2
DEW POINT AS A FUNCTION OF H_2SO_4 CONCENTRATION



THE DOWA'S BASIC ALUMINUM SULFATE-GYPSUM FLUE GAS
DESULFURIZATION PROCESS

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ABSTRACT

The Dowa Mining Company recently developed a basic aluminum sulfate-gypsum process to desulfurize waste gas from smelters, sulfuric acid plants and steam boilers. In this process, SO_2 is absorbed in a clear solution of basic aluminum sulfate in an absorbing tower. The resulting solution is oxidized by air in an oxidizing tower and then neutralized with finely-divided limestone to precipitate gypsum and to regenerate the basic aluminum sulfate solution.

After several tests on a small scale, the first commercial plant ($3,500 \text{ Nm}^3/\text{H}$) was constructed in October 1972 to desulfurize waste gas from a molybdenum sulfide roaster containing 7,500 ppm SO_2 at The Taenaka Mining Company.

³ In June 1974, two large units each treating respectively 140,000 Nm^3/H tail gas from a sulfuric acid plant were started up at the Okayama Works of Dowa.

Another three plants are now under construction. One is for an oil burning boiler, another for iron ore sintering and the third for an converter of antimonial sulfide converter.

THE DOWA BASIC ALUMINUM SULFATE-GYPSUM FLUE GAS DESULFURIZATION PROCESS

I. History of the Process Development

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Dowa Mining Co., Ltd. is one of the major producers of non-ferrous metals such as copper, zinc, lead, etc., in Japan and engages in mining, smelting and refining, and research in these fields. Also in the field of sulfuric acid manufacturing, Dowa is the largest producer in Japan.

Until 1967 the acid plant type to be constructed were the so-called "single contact type", so Dowa has been investigating and developing method for eliminating sulfur dioxide from acid plant tail gas over the past twenty years. For example, we have been scrubbing the acid plant tail gas with sodium sulfite solution in our Okayama plant for eighteen years and with slaked lime milk in our Aoseka plant for eight years.

Since development of the more efficient "double contact process" for sulfuric acid manufacturing, it seemed unnecessary to treat the acid plant tail gas any more. But in our country, the governmental regulation for preventing air pollution has become stricter year by year, so we have had to eliminate more than 90% of sulfur dioxide even from double-contact acid plant tail gas.

With such background, we have investigated to develop a new desulfurization process using basic aluminum sulfate solution as an absorbent in our Okayama laboratory, the work beginning in 1970.

After many laboratory and pilot plant tests, the commercial plant was built, by request of Tsanaka Mining Co., and has operated successfully from Oct. 1972. Gas conditions are 7,500 ppm SO_2 , 3,500 Nm^3/h , and 100°C . The gas comes from a rotary kiln calciner for MoS_2 fired by natural gas.

We then constructed the two trains to eliminate sulfur dioxide from two double-contact acid plants. This was done at the same time the second 1,350 T/D acid plant was constructed in our Okayama plant in 1974.

Design conditions of each plant are as follows:

Gas volume to be treated:	140,000 Nm^3/hr
Gas temperature:	80°C
Gas compositions:	SO_2 , 600 ppm; SO_3 , 50ppm; O_2 , 5%; N_2 , remainder
Adiabatic gas temperature (ts):	28°C
Removal of SO_2 :	more than 95%
Liquid/gas ratio: (l/Nm^3)	2.5 - 3
Diameter of the absorbing tower:	5.8 m
Packing height:	2 m

These plants have operated successfully since start-up in July 1974, with an average removal efficiency of sulfur dioxide during the twenty months of 99%.

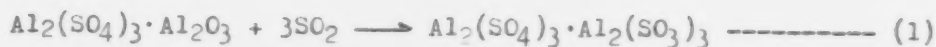
Three more plants are now under construction for various types of waste gas. At the start of this research and development, we aimed to establish a new process which would fix SO_2 in waste gas as gypsum. For the neutralizing reagent, limestone is more preferable to lime because the latter costs about twice as much. Moreover, a simple process and compact equipment with no plugging problems are desirable. After much trial and error, we finally decided on basic aluminum sulfate as the absorbent.

II. Description of the Process

As shown in Figure 1, Dow's "basic aluminum sulfate/gypsum process" consists of the following four simple unit processes, namely;

1) Absorbing

Tail gas is sent to the lower part of an absorbing tower and contacts the basic aluminum sulfate solution countercurrently. Sulfur dioxide contained in the waste gas is absorbed into the solution by the following chemical reaction.



2) Oxidizing

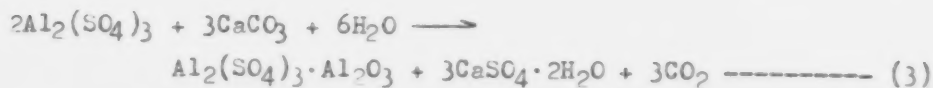
The resulting flows to an oxidizing tower where air is injected through specially designed nozzles. Very fine air bubbles are developed to accelerate the oxidizing reaction. Sulfite in the solution is oxidized to sulfate by the following chemical reaction.



After oxidation, the major part of the solution is recycled to the absorbing tower.

3) Neutralizing

A small part of the oxidized solution is continuously sent to a neutralizing tank where limestone powder is added to neutralize the solution automatically until the basicity (see later definition) of the solution reaches an optimum level.



Then the slurry overflows to a thickener to separate the gypsum crystals. Large crystal size can be attained by recycling a portion of the gypsum slurry from the thickener to the neutralizing tank.

4) Filtering

Underflow from the thickener is pumped to a centrifuge where the gypsum is filtered and washed with water automatically. The thickener overflow, the filtrate, and the washed water are recycled to the absorbing tower. Also, as shown in Figure 1, the flow of all solutions is completely closed, and there is no effluent drained out from the system.

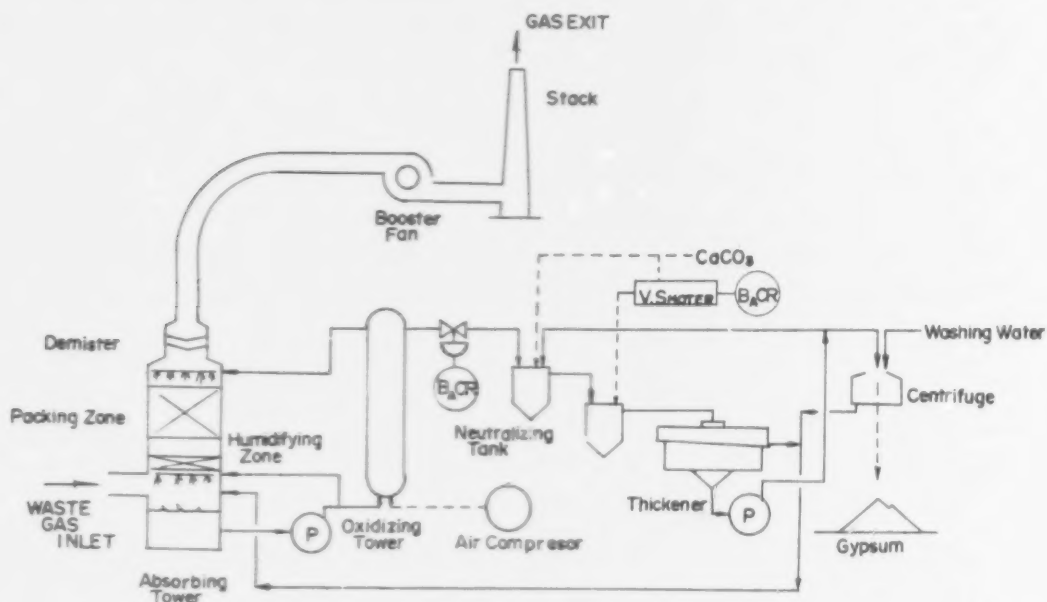
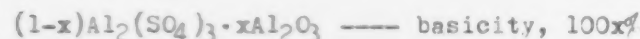


Figure 1 Flow Diagram of Dow's Aluminum Sulfate/Gypsum Process

III. Principle of Absorption

Basic aluminum sulfate solution is a well-known sulfur dioxide absorbent, and was once used in I.C.I.'s process for making liquid sulfur dioxide. This solution is easily made from the liquid aluminum sulfate available on the market by neutralizing with lime powder. Basicity is defined as the degree of neutralization of aluminum sulfate solution, namely:



Aluminum sulfate dissolves easily in water to give a solubility of 360 g/l, equal to 57 g/l aluminum concentration. We have measured the absorption curves at various levels of concentration and basicity of basic aluminum sulfate solution. General speaking higher concentration, higher basicity,

and lower temperature give higher SO_2 absorption, but even at the required operating conditions of lower than maximum concentration and basicity, solution has much better absorption capacity than water.

Figure 2 shows SO_2 absorption curves for lower levels of aluminum concentration. Figure 3 gives curves as a function of basicity and temperature when 1,000 ppm SO_2 is present in gas phase. Even 5.7 g/l aluminum solution has ten times the absorption capacity of water.

Figure 4 indicates the range of aluminum solubility at various basicities. The basicity should be lower than 40% in commercial operation to prevent plugging the packings in the absorbing tower caused by aluminum precipitation from the solution. Also, Figure 5 shows that minimum aluminum loss in the gypsum will be obtained at a concentration of 15 to 20 gpl of aluminum in the solution.

As for the liquid/gas ratio, owing to the good SO_2 absorptivity the ratio can be relatively small with good SO_2 recovery. The L/G ranges from 2.5 to 5.0 l/m³, depending on solution temperature and by SO_2 and O_2 content in waste gas. It will be necessary to use an L/G of 10 or more when flue gas from boilers, and metallurgical plants is being cleaned; the higher gas temperature reduces absorption capacity as compared to sulfuric acid plants. However we found a way to decrease this ratio by addition of a small amount of a certain inorganic catalyst into the absorbent. This catalyst activates the oxygen contained in the flue gas and promotes the oxidation reaction of SO_3 to SO_4 in the solution during the absorbing step. For instance, our pilot plant results indicate that we can use an L/G of 5 to remove more than 95% of the SO_2 when boiler flue gas contains 5% oxygen, and 8 when it contains 3% oxygen.

A rapid rate of oxidation is attained in the weakly acidic solution in the oxidation tower, with a resulting retention time of only a few minutes. We use a newly developed oxidation tower, in the bottom of which are installed special bubble-making devices. And at 3 kg/cm² of pressure is blown into the tower. Oxygen consumption is 60~70% of that fed.

Limestone is ground to a sizedistribution of over 80% through 200 mesh.

Through every step of this process, the aluminum stays in solution and this is fully recoverable. However, because of incomplete washing, some loss is inevitable, but only about 0.5 kg per 1 ton of gypsum. The cost is very small as compared with the total cost.

IV. Problems Encountered and Solutions

1) Taenaka plant

The first plant in Taenaka Mining Co. started in Oct. 1972, treats a waste gas from MoS_2 calcination in a natural gas-fired rotary kiln. A TCA scrubber is used at an L/G of 5, giving 95% SO_2 removal. The solution temperature is 40°C, inlet SO_2 7,500 ppm, H_2O content of gas 4%, oxygen content 10%, gas flow 3,500 Nm³/h, and inlet gas temperature 100°C. Gypsum production is 100 mt/d. There have been no problem with plugging.

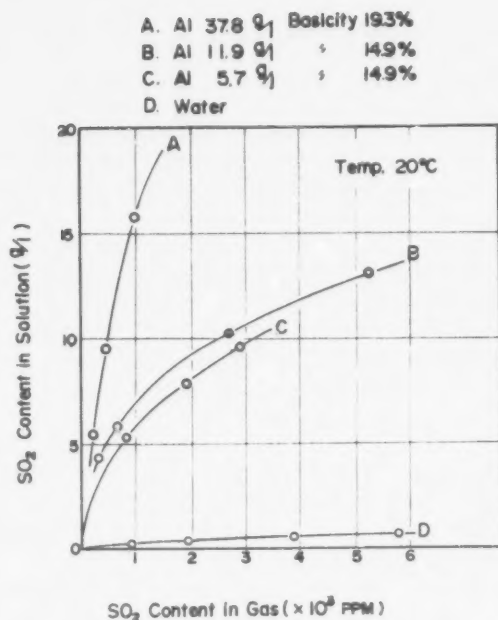


Figure 2 Solubility curves of SO₂ in BAS solutions

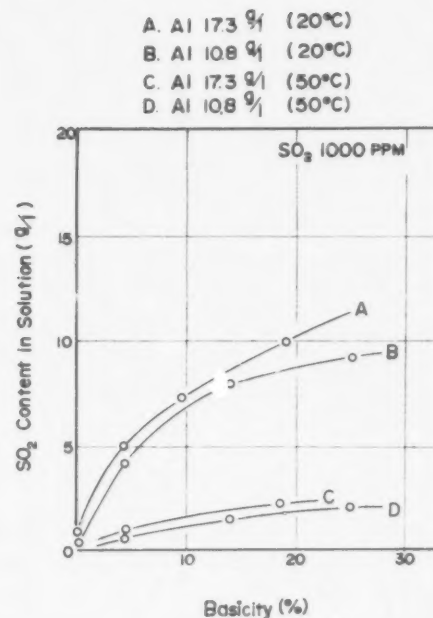


Figure 3 Solubility curves of SO₂ at various temperatures of the solution

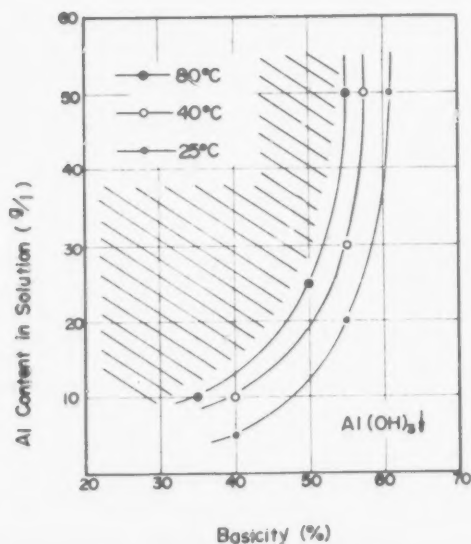


Figure 4 Range of Aluminum being soluble at various basicities of the solution

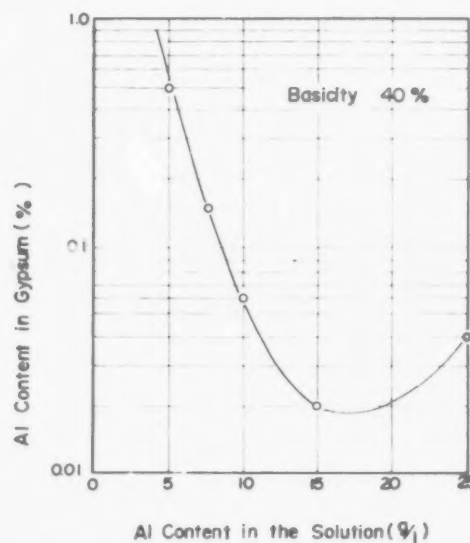


Figure 5 Al loss in gypsum at various Al content in the solution

2) Okayama plant

During the twenty months of operation in our Okayama plant, the main problem we have encountered was how to measure the basicity of the absorbent. First, we measured the pH value of the solution; however the pH didn't vary linearly with basicity. Next we selected electrical conductivity of the absorbent as a possible measure of basicity. This gave us very good results at the beginning, but the magnesium ions coming from the lime added for neutralization gradually accumulated in the solution and interfered because of the much higher conductivity of magnesium ions. At last we found a new method to measure the basicity of the absorbent.

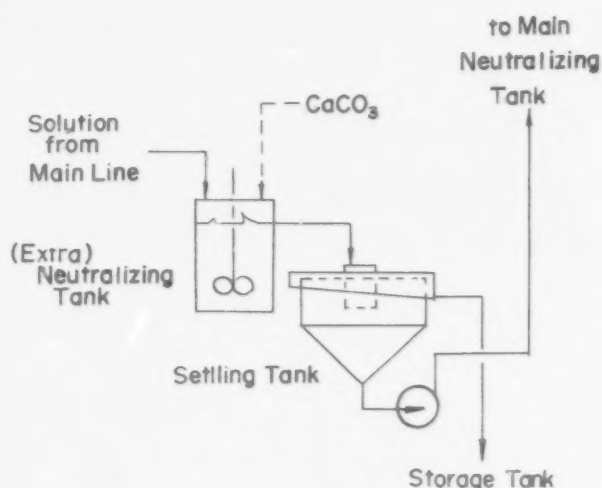


Figure 6 Flow-sheet of de-magnesium unit

Although magnesium ion does not disturb SO_2 absorption, it is necessary to prevent the accumulation of magnesium ions to produce marketable gypsum. We solved this problem by adding a small neutralizing unit to our plant. The additional neutralizing unit consists of a small neutralizing tank and a settling tank as shown in Figure 6. First, a small part of the absorbent is neutralized with excess limestone and the aluminum in the solution is precipitated with the gypsum. Since the magnesium remains in solution, the overflow from the settler can be thrown away to keep the concentration of magnesium ion at a certain level in the absorbent. Underflow from the settler is sent to the main neutralizing tank to avoid loss of aluminum.

V. Cost Analysis

From the results of twenty months of operation, the direct operating cost of our Okayama desulfurization plant is estimated at 20 US cents per 1,000 Nm^3 of gas treated. The items contained in this estimate are as follows;

Plant capacity of 280,000 Nm³/hr and SO₂ 650 ppm.

CaCO₃ ----- 0.81 t/hr (15/t)

Al₂(SO₄)₃ solution (Al₂O₃ 8%) ----- 15 kg/hr (4 d/kg)

Water ----- 7 t/hr

Electric power ----- 7,000 KWH

Operator ----- one person per shift

Figure 7 shows a plant construction cost estimate for boiler flue gas desulfurization in Japan in 1975.

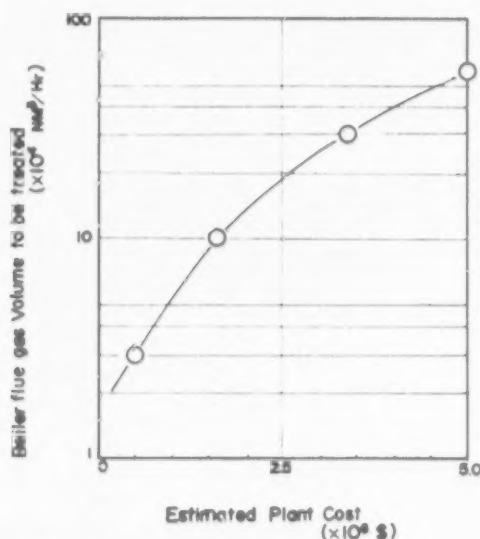


Figure 7 Boiler flue gas desulfurization plant
cost estimation in Japan

VI. Application of our Process

We summarize desulfurization plants using our process as follows:

Completion of construction	Plant name	Gas source	Gas condition					SO ₂ removal efficiency %
			Volume Nm ³ /Hr	SO ₂ ppm	O ₂ %	Temp. °C	ts °C	
Oct. 1972	Taenaka Mining Co.	M	3,500	7,500	10	100	40	95
Jun. 1974	Okayama	A	140,000	600	5	80	28	99
Oct. 1974	Okayama	A	140,000	600	5	80	28	99
under construction	Naikai Co.	B	80,000	1,500	4	250	55	95
under construction	Y	M	50,000	3,000	18	250	56	95
under construction	Nihon Seiko Co.	M	30,000	5,000	19	100	34	95

Note M: Metallurgical furnace
 A: Acid plant
 B: Boiler

VII. Advantages of the Process

Compared with other desulfurization processes, Dowa's "basic aluminum sulfate/gypsum process" has the following advantages.

- 1) Easy operation by a simple process; One stage filtration.
- 2) Stable plant operation because there is no slurry in the absorbing and oxidizing steps.
- 3) Low operating cost because of using limestone as the neutralizing reagent.
- 4) Small equipment size because of low liquid/gas ratio.
- 5) Gypsum with good quality is recovered as by-product.
- 6) No secondary pollution since the system is closed circuit system.

Acknowledgement

The authors are indebted to the management of the Dowa Mining Co., Ltd.

for their kind permission to present this paper. We also grateful to manager S. Koh, former manager T. Otsuka and T. Morikawa and others involved at the Okayama Works; to those involved at the Okayama Research Laboratory; and to manager T. Tomoda and others involved in Dowa Engineering Co., Ltd.

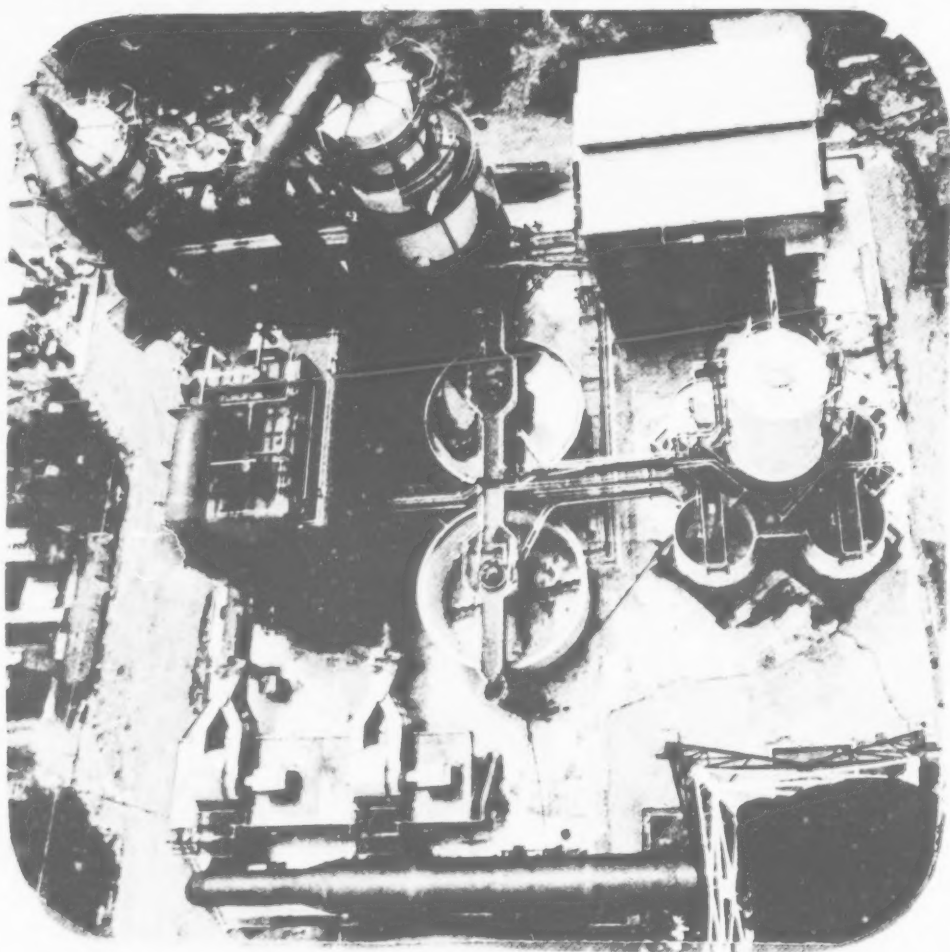


Photo: A bird's-eye view of 280,000 Nm³/Hr (140,000 Nm³/Hx2) plant

CITRATE PROCESS FOR FLUE GAS DESULFURIZATION
A STATUS REPORT

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ABSTRACT

The Federal Bureau of Mines citrate process for removing SO_2 from stack gases contains two basic steps, (1) absorbing SO_2 in a solution of sodium citrate, citric acid, and sodium thiosulfate, and (2) reacting the absorbed SO_2 with H_2S to precipitate elemental sulfur and regenerate the citrate solution for recycle. The Bureau's research and development of the citrate process includes the operation of a pilot plant to assess feasibility for flue gas desulfurization. The pilot plant treats 1,000 cubic feet per minute of a 0.5-percent SO_2 flue gas from a lead sintering furnace, removes more than 95 percent of the SO_2 , and produces about 600 pounds of sulfur per day. It has operated for a total of about 4,500 hours and produced more than 50 net tons of sulfur. Plans are being made to demonstrate the citrate process on a 50- to 100-megawatt (MW) base-loaded electrical utility burning high-sulfur coal. Operating costs for a citrate plant, including capital charges, installed at a 1,000-MW base-loaded electric utility burning high-sulfur coal are estimated to be about 3.8 mills per kilowatt-hour.

CITRATE PROCESS FOR FLUE GAS DESULFURIZATION, A STATUS REPORT

INTRODUCTION

In 1968, the Bureau of Mines Salt Lake City Metallurgy Research Center started research on flue gas desulfurization with particular emphasis on control of SO_2 emissions from the nonferrous smelting industry. Pioneering research had indicated that flue gas desulfurization might be achieved effectively by the absorption of sulfur dioxide (SO_2) in a suitable solution, followed by reaction of the absorbed SO_2 with gaseous hydrogen sulfide (H_2S) to precipitate sulfur and regenerate the solution for recycle. After a year of screening many possible reagent combinations of inorganic and organic solutions, it was established that an aqueous solution of citric acid and sodium citrate was an effective absorbent for SO_2 . Among the desirable characteristics affecting the choice of citrate were its good chemical stability, low vapor pressure, and adequate pH buffering capacity, and the purity and physical character of the precipitated sulfur.

As first studied in the laboratory, the citrate process comprised (1) absorbing SO_2 in citrate solution, (2) reacting the absorbed SO_2 with H_2S , (3) filtering and melting the precipitated sulfur, and (4) recycling the regenerated citrate solution to the SO_2 absorption step. Preparation of the H_2S required for the precipitation step of the citrate process was studied separately. Hydrogen sulfide was generated by reacting recycle sulfur, natural gas, and steam over an alumina catalyst.

Subsequently, in 1970 and 1971, a pilot plant to remove SO_2 from flue gas from a copper reverberatory furnace was constructed and operated jointly by the Bureau of Mines and the Magma Copper Co. This plant, located at the San Manuel smelter in Arizona, treated 300 standard cubic feet per minute (scfm) of gas containing 1.0 to 1.5 percent SO_2 and consistently removed 93 to 99 percent of the SO_2 . Results of the initial laboratory and pilot plant research were reported in 1970 and 1971 (3, 8).^{1/}

The preliminary Bureau of Mines laboratory and pilot plant research demonstrated that the citrate process is capable of substantially complete removal of SO_2 from industrial waste gases. Most of the SO_2 is converted to sulfur with less than 1.5 percent converted to sulfate regardless of the SO_2 and oxygen content of the feed gas. The citrate process produces an elemental sulfur end product that can be marketed or stored with a minimum of environmental disturbance.

After the encouraging preliminary results, two other pilot plant investigations were undertaken to obtain data for engineering evaluation and cost estimates. One pilot plant independently built and operated by Arthur G. McKee and Co., Peabody Engineered Systems, and Pfizer, Inc., at Terre Haute, Ind., is described in four publications (1, 2, 4, 10). This pilot plant operation treated a stack gas from a coal-fired steam-generating station simulating a utility application. After several modifications to arrive at a final equipment configuration, the pilot plant operated from March 15 to September 1, 1974, logging 2,300 operating hours. The longest sustained run was 180 hours. The Terre Haute pilot plant consistently removed 95 to 97 percent of the SO_2 from flue gas containing 0.1 to 0.2 percent SO_2 . The other pilot plant was constructed by the Federal Bureau of Mines and operated jointly by the Bureau of Mines and The Bunker Hill Co. at the lead smelter in Kellogg, Idaho. The design, construction, and operation of the Bureau's Bunker Hill citrate pilot plant are described in three publications (5-7).

^{1/} Underlined numbers in parentheses refer to the list of references at the end of this report.

The present report describes the further operation of the Bureau's Bunker Hill citrate pilot plant operation, process development, plans for a 50- to 100-MW-scale citrate process demonstration plant, and estimated costs for a 1,000-MW base-loaded electrical utility burning high-sulfur coal based on the pilot plant operation.

PROCESS DESCRIPTION

As a result of further process developments, the citrate process, as now envisioned and shown in figure 1, comprises the following steps:

1. The SO_2 -bearing gas is cooled to between 45° and 65° C (113° and 149° F) and cleaned of sulfuric acid (H_2SO_4) mist and solid particles.
2. The SO_2 is absorbed from the cooled and cleaned gas by a solution of sodium citrate, citric acid, and sodium thiosulfate.
3. Absorbed SO_2 is reacted with H_2S at about 65° C (149° F) and atmospheric pressure to precipitate elemental sulfur and regenerate the solution for recycle.
4. Sulfate is removed from a slipstream of regenerated recycle citrate solution by cooling the solution and crystallizing Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), which is removed by filtration and then washed.
5. Sulfur is separated from the solution by oil flotation and melting.
6. The H_2S for step 3, if not otherwise available, is made by reacting two-thirds of the recovered sulfur with natural gas and steam.

CHEMISTRY OF THE PROCESS

Absorption of SO_2 in aqueous solution is pH dependent, increasing at higher pH. Because dissolution of SO_2 forms bisulfite (HSO_3^-) ion with resultant decrease in pH by the reaction



the absorption of SO_2 in aqueous solution is self-limiting. However, by incorporating a buffering agent in the solution to inhibit pH decrease, high SO_2 loadings and substantially complete SO_2 removal from waste gases can be attained. The principal function of the citrate or other carboxylates that have been tested is to serve as a buffering agent during SO_2 absorption.

The chemistry for the production of sulfur (S^0) and regeneration of absorbent by reacting H_2S with the SO_2 in the aqueous solution is complex, but the overall reaction is as follows:



Actually, thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and polythionates are found in solution at equilibrium concentrations after several SO_2 -absorption and H_2S -regeneration cycles. Oxidation of SO_2 in the aqueous solution is sharply depressed by the complexing of HSO_3^- from reaction 1 by the $\text{S}_2\text{O}_3^{2-}$ ion, according to the following reaction:



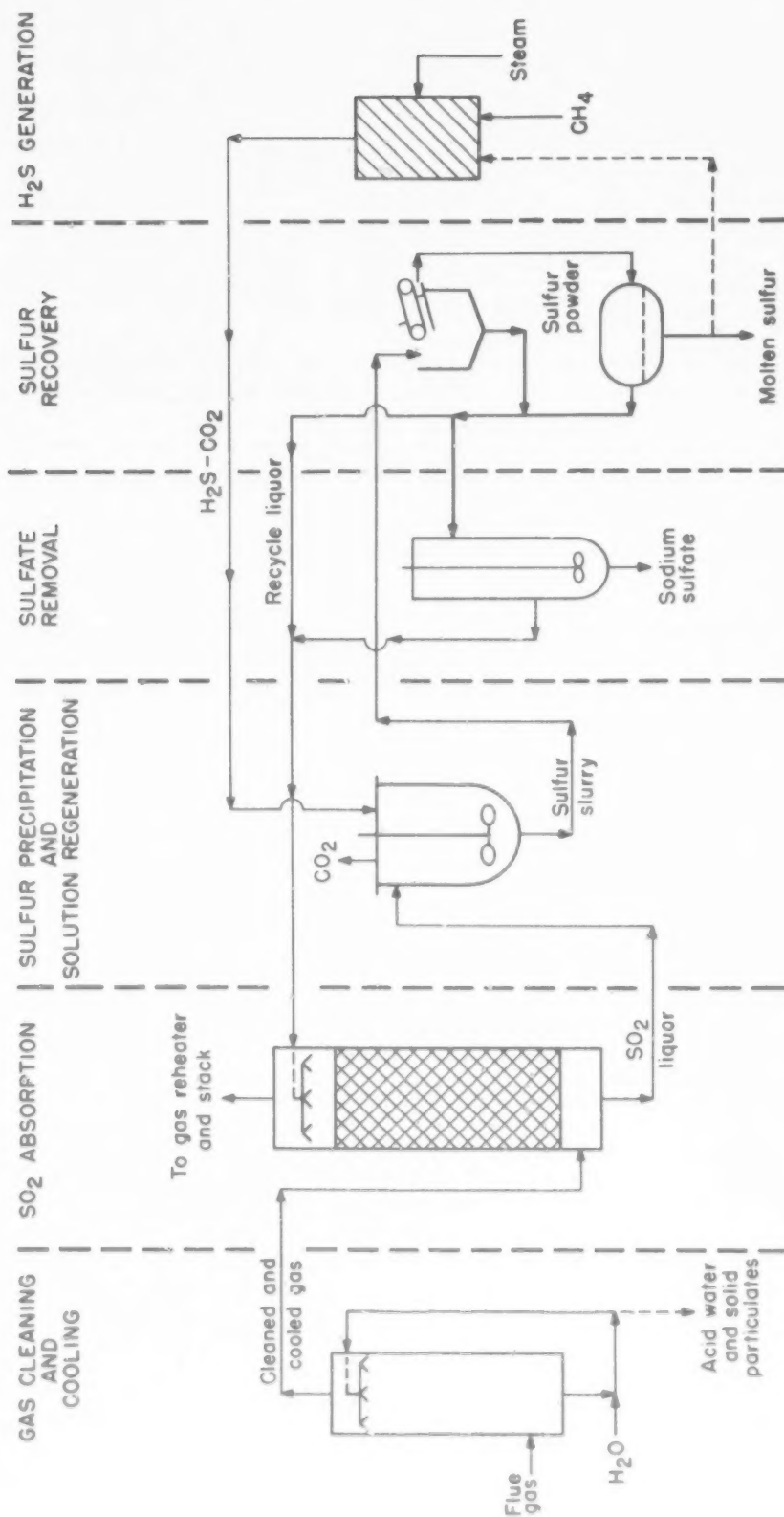


FIGURE 1.-Generalized citrate process flowsheet.

D-2614-SL

To insure satisfactory operation of the system on startup, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) is added to the initial absorbing solution.

Hydrogen sulfide for regenerating the absorbent and precipitating elemental sulfur can be produced by reacting sulfur with methane (CH_4) and steam (H_2O), as shown in reaction 4:



Other reducing gases, such as hydrogen and carbon monoxide, individually or combined, can be used in place of methane.

More detailed information on the chemistry of the citrate process is provided in a Bureau of Mines publication (9) and a paper presented at the American Chemical Society National Meeting in April 1974 (4).

BUNKER HILL CITRATE PILOT PLANT

Details of construction of the Bunker Hill citrate pilot plant are described in previous Bureau of Mines papers (5-7). The nominal capacity of the pilot plant is 1,000 scfm of 0.5 percent SO_2 gas yielding about 600 pounds of sulfur per day. A block diagram of the complete pilot plant is shown in figure 2. The plant will be discussed in three sections:

1. Gas cooling and cleaning required prior to SO_2 absorption.
2. Citrate absorption system, including SO_2 absorption, SO_2 reduction to regenerate the absorbing solution and precipitate sulfur, and sulfur recovery.
3. Generation of the H_2S required for the reduction of absorbed SO_2 .

Between February 1974 and November 1975, the citrate pilot plant operated for more than 4,500 hours and produced more than 50 net tons of sulfur. The only anticipated further operation will be a 4- to 6-week campaign in the spring of 1976.

Gas Cooling and Cleaning

A slipstream of the lead smelter sinter plant tail gas, which contains dust, acid mist, and from 0.3 to about 1 percent SO_2 , was used as pilot plant feed. This sinter tail gas normally passes through a baghouse and then is discharged to the atmosphere through Bunker Hill's main stack. To simulate conventional lead smelter practice, the gas cooling and cleaning section was designed to recover most of the valuable dust from 1,000 scfm of the tail gas in a baghouse, cool the gas in a packed wet scrubber, and remove H_2SO_4 mist and traces of particulate matter with a wet electrostatic precipitator. One of the goals in the pilot plant operation was to determine the minimum gas cleaning requirement compatible with the citrate process.

Shakedown runs of the gas cooling and cleaning section of the pilot plant showed that the slipstream of sinter plant tail gas had an SO_2 concentration of up to 2 percent, which was higher than anticipated and had to be diluted with air to avoid exceeding the pilot plant's capacity of 1,000 scfm of 0.5 percent SO_2 gas. The gas also required heating to prevent acid mist condensation and corrosion in the baghouse. After making these changes, the gas cooling and cleaning section functioned satisfactorily and was operated with the SO_2 absorption-regeneration section of the pilot plant.

Some pilot plant operations were conducted on sinter plant tail gases that were diluted below 0.5 percent SO_2 ; these would be similar in SO_2 concentration to coal-fired powerplant flue gases. During these operations the sinter plant tail gases were diluted to between 0.07 and 0.13 percent SO_2 .

During the operation of the pilot plant, investigations were made of the effectiveness of and requirements for the gas cooling and cleaning equipment. The baghouse was used during all of the operation. The effect of bypassing either the electrostatic mist precipitator or both the electrostatic mist precipitator and the packed wet scrubber on SO_2 absorption and sulfate ($\text{SO}_4^{=}$) buildup in the citrate scrubbing solution was studied.

Gas samples from the gas cooling and cleaning section showed that the sinter plant tail gas contained about 3 grains of dust per cubic foot (7.0 grams per cubic meter). When the tail gas was diluted, the average dust loading was about 0.6 grain per cubic foot (1.4 grams per cubic meter). Gas sampling results showed that over 99.6 percent of this dust was removed in the baghouse, leaving less than 0.002 grain of dust per cubic foot (4.6 milligrams per cubic meter). Gas samples for dust contained in the packed wet scrubber or the electrostatic mist precipitator were not taken. However, these pieces of gas cleaning equipment were assumed to remove some dust.

Analysis showed that the dilute sinter plant tail gas contained 0.02 to 0.5 milligram SO_3 per cubic foot instead of the 2 milligrams it was originally estimated to contain. Although this low SO_3 content is equal to, or less than, the guaranteed SO_3 content of the gas at the outlet of the electrostatic mist precipitator, about two-thirds of the SO_3 from the diluted sinter plant tail gas was removed by the combination of cleaning equipment. The design intention of the gas cooling and cleaning section was to use water sprays to precondition the tail gas and form H_2SO_4 mist. The water sprays were not used owing to the unusual method of operation, which was to dilute and heat the tail gas. With little H_2SO_4 mist formed, it was doubtful that the electrostatic mist precipitator removed much SO_3 . Besides removing some SO_3 , the packed wet scrubber, when used, provided the necessary gas cooling. During one period, the packed wet scrubber was bypassed to determine the effect of a hot dry gas on the SO_2 absorption. The only detrimental effect observed was an increased $\text{SO}_4^{=}$ buildup in the scrubbing solution. This indicates that most of the SO_3 removal occurred in the packed wet scrubber, as described in more detail in the absorption-regeneration section of this paper. Despite the problems encountered, the gas cooling and cleaning equipment satisfactorily cleaned and cooled the gas for the SO_2 removal step of the citrate process.

Citrate Absorption

Following gas cooling and cleaning, as shown in figure 2, the SO_2 -bearing flue gas stream passed through a 2.5-foot-diameter by 30-foot-high packed absorption tower countercurrent to the citrate solution, in which over 95 percent of the SO_2 was usually absorbed. The absorption tower contains three 6-foot sections packed with 1-inch polypropylene Intalox^{2/} saddles and a stainless steel mist eliminator.

From the absorption tower, the citrate solution flowed by gravity to closed, stirred vessels for reaction with two-thirds ton of H_2S per day to form 1 ton per day of elemental sulfur. From one to three 100-gallon stainless steel reactor vessels, which were arranged for countercurrent flow of citrate solution and H_2S

^{2/} Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

generator product gas, were used for the SO_2 reduction reaction-sulfur precipitation step. A slurry containing 1 to 3 percent solids of elemental sulfur in the regenerated citrate solution overflowed the reactors and passed through a common header to a stainless steel reactor effluent tank. From this tank, the dilute slurry was pumped to a 100-gallon conditioner tank where kerosine or other hydrocarbon oil was added for the sulfur flotation-separation step.

From the conditioner tank the slurry flowed to a specially designed sulfur flotation skimming device resembling an Esperanza drag classifier. The sulfur separated from the oil-conditioned slurry by floating to the surface as a 35- to 45-percent-solids product. Some pilot plant operation was conducted using air flotation in which no kerosine was added to the dilute slurry. Such flotation produced a wet sulfur product of about 8 percent solids. Both oil and air flotation satisfactorily separated the sulfur from the bulk of the citrate solution, leaving clear regenerated citrate for recycle to the absorption tower. The sulfur was skimmed off the surface of the citrate solution, pulled up an inclined chute, and discharged to a conical storage bin.

Regenerated citrate solution from the feed well of the sulfur skimmer passed to a 300-gallon absorber feed tank. Citrate solution from the absorber feed tank was pumped through parallel backwash clarification filters and a water-cooled heat exchanger to the absorption tower.

On day shift only, the sulfur float product was withdrawn from the storage bin and pumped by a Moyno positive-displacement auger-type pump through a single-tube, steam-jacketed heat exchanger where the sulfur was melted at about 135°C (275°F). Molten sulfur and citrate solution passed into a closed settler tank at 135°C under a pressure of 35 psig. Part of the molten sulfur was tapped from the bottom of the autoclave settler and cast in 100-pound blocks; the balance was pumped to the H_2S generating plant. Citrate solution and the oil used for flotation were withdrawn from the top of the settler and then passed through a sulfur knockout pot and a water-cooled heat exchanger into a decanting vessel for separation and reuse. Citrate solution from this tank drained into the absorber feed tank.

The pilot plant was completely instrumented and controlled from a panel mounted in a 40-foot-long instrument trailer that was connected to the pilot plant building and also served as an onsite laboratory.

An incinerator was provided outside the main building to burn H_2S vented from the system or released under emergency or upset conditions. In a commercial plant, the offgas from the incinerator would be returned to the gas stream entering the absorber, but in the pilot plant this offgas was vented to the smelter stack.

Operation of the Bunker Hill citrate pilot plant was started on February 15, 1974. The plant operated for a total of 4,500 hours through November 1975, and produced about 50 net tons of bright yellow, high-quality sulfur. During about 450 hours of this operation, a glycolate scrubbing solution was satisfactorily substituted for the citrate solution.

Because of interruptions resulting from irregular operation of the lead smelter sinter plant with frequent unavailability of feed gas, the longest continuous operation was about 265 hours.

Laboratory tests preceding pilot plant studies indicated that a pH of about 4.5 was needed for good absorption. During continuous campaigns in late summer 1974 when only one of the three precipitation reactors was being used, the pH of the recycled citrate solution dropped below 4.5, and SO₂ absorption efficiency subsequently decreased. As the pH dropped from 4.5 to about 4.0, the SO₂ removal efficiency at the design gas flow of 1,000 scfm of 0.5 percent SO₂ feed gas at 45° C (113° F) dropped from 99 to 85 percent. During this time, the SO₂ content of the offgas from the pilot plant increased from about 30 parts per million (ppm) to 750 ppm. Laboratory regeneration tests on samples of the pilot plant citrate solution showed that a combination of low pH, high polythionate content, and low thiosulfate content resulted from incomplete regeneration of the absorbent solution. The principal cause of incomplete regeneration was found to be insufficient retention time of H₂S gas in the single sulfur precipitation reactor. Apparently, slightly more contact time than that provided in one reactor was necessary for effective utilization of the H₂S. If the H₂S-SO₂ reaction for producing elemental sulfur is not allowed sufficient time, more polythionates, principally in the form of polythionic acids, are produced, permitting the pH of the solution to drop. Low solution pH causes two problems, the more critical of which is a drop in the SO₂ absorption efficiency. This problem was solved by (1) increasing the contact time of H₂S with the loaded liquor by using two reactors with countercurrent flow of H₂S and citrate solution, (2) adding sodium thiosulfate to bring the concentration back up to the desired level, and (3) adding sodium carbonate to neutralize the sulfuric acid in the plant solution. These measures were successful in regenerating the pH at 4.5 and restoring high SO₂ absorption capability to the solution. In subsequent campaigns, the indicators of incomplete regeneration (low pH, high polythionates, and low thiosulfate) were closely monitored. The second problem was thermal decomposition of thiosulfate in the sulfur-melting system, which accelerates at pH 4 or below, thus increasing the sulfate concentration of the solution. In practice, this would require additional sodium carbonate for neutralization and purging of the additionally formed sodium sulfate from the system.

In the early stages of plant operation, excess H₂S absorbed in the citrate solution resulted in cloudy recycle solution being recovered from the kerosine flotation step, apparently due to delayed precipitation of colloidal sulfur. Some of the absorbed H₂S escaped at times from the sulfur skimmer into the plant building; this was corrected by using the second or third stirred reactor as a delay tank to allow more contact time with the H₂S and bypassing about 5 volume-percent of the SO₂-loaded solution from the absorption tower to the reactor effluent tank, where it reacted with the excess absorbed H₂S. These measures have resulted in consistently clear citrate solution from sulfur flotation for recycling to the absorption tower and have stopped the escape of H₂S from the sulfur flotation unit.

During precipitation of sulfur with H₂S gas, sulfur buildup along the walls of the stainless steel reactors or on the impellers was minimal when the tip speed of the impellers was at least 900 feet per minute. However, sulfur plugs were a chronic problem in the pipelines between reactors and required periodic cleanout.

The kerosine conditioner tank operated well with no sulfur buildup at the design liquid flow rate when the impellor tip speed was at least 700 feet per minute. Initially, some trouble was experienced with holdup of floated sulfur in the freeboard of the tank. This required an occasional cleanout of the 3-inch-diameter overflow line to the skimmer. However, the addition of a second impellor operating just beneath the liquid surface prevented buildup of the large lumps of powdery floated sulfur that were blocking the overflow line.

Some plugging problems were encountered in the citrate solution lines from the autoclave settler, apparently because of sulfur being dissolved in the kerosine flotation reagent and then crystallizing out upon cooling. Such problems were reduced by installing an additional knockout, heat-exchanger vessel. The automatic sulfur level control, which controls the molten sulfur flow from the autoclave settler, gave some trouble, and at times scrubbing solution was transferred through the molten sulfur pipeline to the H₂S generator when the automatic control malfunctioned. This scrubbing solution caused plugging in the liquid sulfur lines and pumps. Accurate material balances to determine citrate losses could not be made whenever such scrubber solution losses occurred.

Table 1 summarizes results obtained under steady-state continuous operation at gas flow rates between 1,000 and 1,300 scfm and SO₂ concentrations of 0.07 to 0.55 percent. The absorption temperatures ranged from 34° to 58° C (93° to 136° F). Citrate solution flow rate in the absorber was 7.5 and 10 gallons per minute, citrate concentration was 0.5 M, the sodium-to-citric acid molar ratio in the citrate solution was 2:1, and the pH of the citrate feed solution to the absorption tower was about 4.4 to 4.8.

TABLE 1. - Results of Bunker Hill citrate pilot plant operation, February 1974-October 1975

Feed gas		Citrate solution		Absorption temperature, ° F	Offgas concentration, ppm SO ₂	SO ₂ removal efficiency, pct
Concentration, pct SO ₂	Flow, scfm	Flow, gal/min	Loading, g/l SO ₂			
0.07	1,000	7.5	1.9	93	2	99.7
.11	1,100	7.5	3.2	109	5	99.6
.13	1,300	7.5	4.1	136	61	95.3
.52	1,000	10	10.7	100	44	99.1
.55	1,000	10	11.2	96	46	99.2

The citrate pilot plant was designed to treat 1,000 scfm of 0.5 percent SO₂ gas at 113° F with 10 gallons per minute of 0.5 M citrate solution. Because of the unusual mode of operation of the gas cooling and cleaning section of the pilot plant, the gas temperature at the inlet of the SO₂ absorption tower ranged from 90° to 100° F. As shown in table 1, the SO₂ removal efficiency was 99.2 percent with the offgas containing 46 ppm when treating 1,000 scfm of 0.55 percent SO₂ gas at 96° F and using 10 gallons per minute of 0.5 M citrate solution. However, preliminary test results of the citrate absorption section, which were reported previously (6), showed that under design conditions (1,000 scfm of 0.5 percent gas at 113° F and 10 gallons per minute of 0.5 M citrate solution), an SO₂ removal efficiency of 99.4 percent and an offgas containing less than 30 ppm SO₂ were obtained. For this test, the solution loading of 9.8 grams SO₂ per liter represented 55 percent of the maximum equilibrium loading of 0.5 M citrate solution at the absorption temperature of 113° F. Preliminary test results also showed that the SO₂ removal efficiency exceeded 96 percent and the offgas contained less than 200 ppm SO₂ even when the feed gas temperature was increased to 65° C (149° F).

As shown in table 1, excellent results were also obtained when treating gases containing from 0.07 to 0.13 percent SO₂, which would be similar in SO₂ concentration to coal-fired powerplant flue gases. When treating 1,100 scfm of 0.11 percent gas at 109° F and using 7.5 gallons per minute of 0.5 M citrate solution, an SO₂ removal efficiency of 99.6 percent and an offgas containing 5 ppm SO₂ was obtained. The solution loading of 3.2 grams SO₂ per liter represents about 50 percent of the maximum equilibrium loading of 0.5 M citrate solution at the

absorption temperature of 109° F. Test results also show an SO₂ removal efficiency exceeding 95 percent and offgas containing 61 ppm SO₂ when treating lower strength gases at higher gas flow rate, even when the gas temperature was increased to 58° C (136° F). The solution loading of 4.1 grams SO₂ per liter under these conditions represents over 80 percent of the maximum equilibrium loading of 0.5 M citrate solution at the 136° F absorption temperature. At the design capacity of the plant, a gas flow rate of 1,000 scfm and a solution flow rate of 10 gallons per minute, the total pressure drop through the absorption tower was 6 inches of water.

In the early stages of Bureau research to develop the buffered SO₂-H₂S process for removing SO₂ from stack gases, laboratory tests indicated that other carboxylate solutions could be substituted for citrate solution as the buffering agent. Citric acid was initially chosen for development of the process because of its chemical stability, low vapor pressure, and good pH buffering capacity, and the purity and physical character of the precipitated sulfur. Other carboxylates tested appeared to have about the same properties as citric acid and cost less in some cases, but in the closed system projected, with slight solution or decomposition loss, the carboxylate price seemed relatively unimportant. However, depending on reagent losses and relative price, the use of less costly carboxylates might become worthwhile.

One of the more promising of the other carboxylate systems investigated in the laboratory was a solution of sodium glycolate, glycolic acid, and sodium thiosulfate. Citric acid is nontoxic and is, in fact, used in many food products, whereas the biological effects of glycolic acid are not well understood. However, glycolic acid is one-third the molecular weight and less than half the cost of the citric acid. Because of these possible advantages it was also tried in the Bunker Hill pilot plant. Table 2 summarizes results obtained under steady-state continuous operation at gas flow rate of 1,000 scfm and SO₂ concentrations of 0.2 to 0.5 percent when using a sodium glycolate scrubbing solution. The absorption temperature averaged about 38° C (100° F). Glycolate solution flow rate in the absorber was 7 and 10 gallons per minute, glycolate concentration was about 0.75 M, the sodium-to-glycolic acid molar ratio in the glycolate solution was 0.9:1, and the pH of the glycolate feed solution to the absorption tower ranged from 4.2 to 4.3.

TABLE 2. - Results of Bunker Hill pilot plant operation
(glycolate), October-November 1975

Feed gas concentration, pct SO ₂	Glycolate solution			Offgas concentration, ppm SO ₂	SO ₂ removal efficiency, pct
	Flow, gal/min	Loading, g/l SO ₂	Regenerated, pH		
0.21	10	4.6	4.3	19	99.1
.41	10	8.5	4.2	155	96.2
.42	7	12.3	4.3	187	95.6

The test results show that the glycolate solution may be used to effectively remove SO₂ from flue gases. When treating 1,000 scfm of 0.41 percent gas at 100° F and using 10 gallons per minute of 0.75 M glycolate solution, an SO₂ removal efficiency of 96.2 percent and an offgas containing 155 ppm SO₂ were obtained. The solution loading of 8.5 grams SO₂ per liter represents about 50 percent of the maximum equilibrium loading of 0.75 M glycolate solution at the absorption temperature of 100° F. Results also show that the SO₂ removal efficiency exceeded 95 percent and the offgas contained less than 200 ppm SO₂ even when the solution loading was

increased to 12.3 grams per liter, which represents over 66 percent of the maximum equilibrium loading of an 0.75 M glycolate solution at the absorption temperature of 100° F. Excellent results were obtained when treating a gas containing 0.21 percent SO₂, which would be similar in SO₂ concentration to a coal-fired powerplant flue gas. In this test, an SO₂ removal efficiency of 99.1 percent and an offgas containing 19 ppm SO₂ were obtained. The solution loading of 4.6 grams SO₂ per liter represents about 30 percent of the maximum equilibrium loading of 0.75 M glycolate solution at the absorption temperature of 100° F.

The SO₂ reduction reaction-sulfur precipitation reactor circuit effectively regenerated the citrate or glycolate solutions using the dilute (56 to 79 percent) H₂S gas product of the H₂S generator. Test results showed that to obtain 96 percent utilization of H₂S in a dilute gas required an average solution retention time of about 40 minutes and an agitator impellor peripheral speed of 900 feet per minute.

The flotation circuit operated satisfactorily at the design capacity of 1 ton of sulfur per day. A powderlike sulfur product of about 40 percent solids was produced by adding 28 pounds of kerosine (4 gallons) per long ton of precipitated sulfur. At this kerosine addition rate, very little kerosine was recovered. About 75 percent of the kerosine loss was attributed to volatilization from the hot sulfur slurry in the kerosine conditioner and sulfur skimmer. The other 25 percent of the kerosine was contained in the sulfur product and sulfur recycled to the H₂S generator. To eliminate the necessity for kerosine addition, some pilot plant operation was conducted using air flotation. Air flotation satisfactorily separated the sulfur from the bulk of the scrubbing solution; however, air flotation produced a wet sulfur product of about 8 percent solids.

The sulfur melting step functioned satisfactorily at the design capacity, 250 to 300 pounds of sulfur per hour, when melting kerosine-floated sulfur. When melting air-floated sulfur, the sulfur melter-settler did not provide enough residence or settling time to make a clean separation between the liquid sulfur and the scrubbing solution at design capacity.

The sulfur produced by the Bunker Hill pilot plant has been bright yellow and of better than 99.5 percent purity. Carbon content, when using kerosine flotation, ranged from 0.2 to 0.3 percent, and when using air flotation, was less than 0.04 percent. Ash content was about 0.03 percent.

During operation of the Bunker Hill pilot plant, the SO₄⁼ buildup rate, which occurs from the absorption of SO₃, oxidation of SO₂, and oxidation of S₂O₃⁼, was determined to be between 1.3 and 1.5 percent of the SO₂ in the feed gas. This is quite low considering that the feed gas, which is predominately air, contained about 20 percent O₂. Although the SO₄⁼ buildup rate was not affected by bypassing the electrostatic mist precipitator, the higher rate, 1.5 percent, did occur when the gas cooling and cleaning packed wet scrubber was bypassed. Laboratory studies show that about one-third of the SO₄⁼ buildup occurs by oxidation of S₂O₃⁼ in the sulfur melter. The highest sulfate concentration in the plant was about 75 grams per liter. However, this figure is not representative of the greater sulfate buildup expected because of solution losses during pilot plant operation, which required a makeup of fresh scrubbing solution.

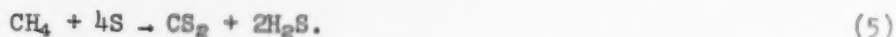
The most important chemical makeup requirements for the SO₂ absorption-regeneration section of the pilot plant include citric acid, sodium carbonate, and kerosine. The average of many citrate loss tests showed that about 19 pounds of citric acid was lost per net long ton of sulfur produced. A sodium carbonate addition of

about 100 pounds per net long ton of sulfur product was required to neutralize sulfuric acid produced in the process. Although the kerosine consumption in the pilot plant was about 85 pounds per net long ton of sulfur produced, it may be possible to recover the 75 percent that is volatilized in the flotation circuit.

H₂S Generation

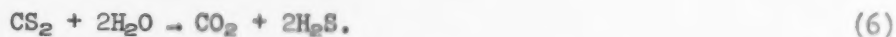
The H₂S generator indicated as a single block in figure 1 is depicted in some detail in the flow diagram, figure 3. Solid lines in this diagram indicate flows for a two-stage reaction considered to be a proven process. This two-stage operation is discussed first. The dashed lines indicate provision to bypass reactor 2 for later experimentation with a single-stage reaction. The design capacity of the plant was 0.4 to 1.25 tons of H₂S per day.

Molten sulfur produced in the pilot plant was transferred to a sulfur feed tank from which it was pumped through a filter to remove carbon and ash impurities and then to a gas-fired superheater. The sulfur was vaporized and superheated to about 730° C (1,350° F). Natural gas containing about 92 percent methane and 6 percent heavier hydrocarbons heated to 650° C (1,200° F) in another gas-fired superheater joins with the hot sulfur vapor ahead of reactor 1. The first stage of the sulfur-methane-steam reaction to produce H₂S and CS₂ takes place in the presence of a catalyst in this reactor according to the following equation:

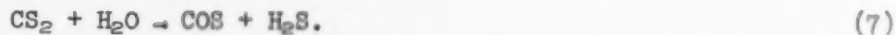


The H₂S-CS₂ reactor product gas was first air-cooled to about 315° C (600° F) and then further cooled in a steam-cooled heat exchanger to about 150° C (300° F). Excess sulfur was condensed in the reactor product cooler and was removed from the gas mixture in the first sulfur knockout vessel.

Steam was superheated to 425° C (800° F) in a gas-fired steam superheater and then blended with the cooled H₂S-CS₂ gas prior to entering reactor 2. In this reactor, the CS₂ was hydrolyzed to H₂S and CO₂ in a catalyst bed at 370° C (700° F) according to the following reaction:



Another important reaction that occurs during CS₂ hydrolysis forms COS according to the following reaction:



In the laboratory it was determined that reaction 7 was depressed by feeding excess steam and favored by high reaction temperatures.

A steam-cooled heat exchanger cooled the reactor 2 product gas to 150° C (300° F) to condense any free sulfur. The condensed sulfur was removed in two additional knockout tanks. Sulfur collected in all three knockout vessels was periodically drained to the sulfur feed tank. Product gas from the second reactor containing H₂S, CO₂, and some water vapor was cooled to about 65° C (149° F) in a water-cooled heat exchanger and then flowed to the SO₂ absorption and sulfur recovery section of the citrate pilot plant.

The major problem experienced during the pretesting of the H₂S generator was the overheating and damage of the sulfur vaporizer piping when attempting to provide the heat required for efficient reaction in reactor 1. This problem was solved by shortening the process piping between the superheaters and reactor 1, adding insulation to process piping and reactor 1, and feeding an excess of sulfur.

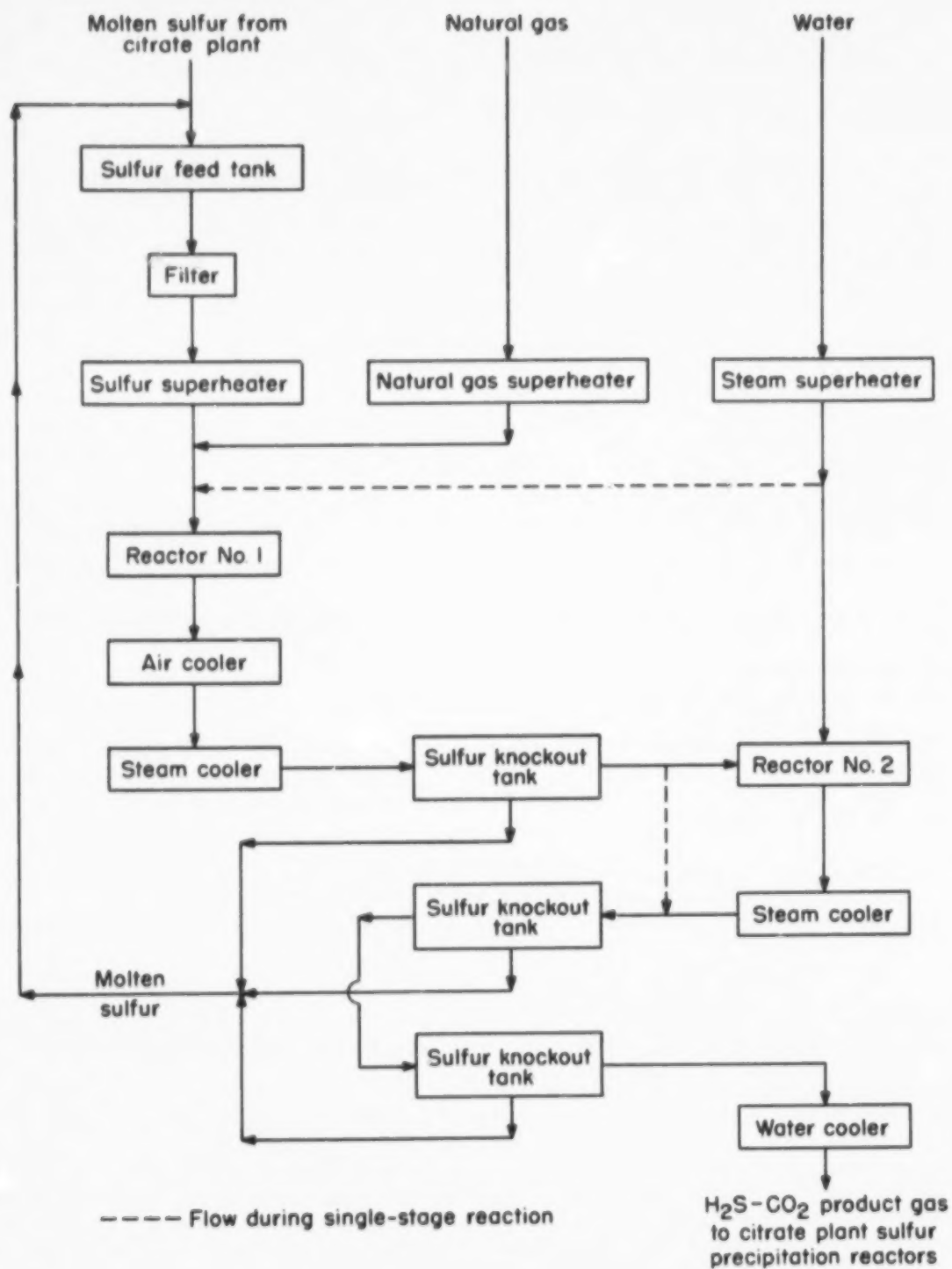


FIGURE 3.-Bunker Hill citrate pilot plant-H₂S generation section.

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After pretesting, the operation of the H_2S generator was integrated with the operation of the SO_2 absorption-regeneration section. Two serious operating problems developed during continuous operation. The first, and probably the most chronic, problem was sulfur plugging of the cold H_2S product lines and valves because sulfur vapor was not effectively removed from the product gas. The second problem was carbon plugging of the first reactor and the piping carrying superheated natural gas and superheated sulfur. This was due to natural gas cracking to form elemental carbon. The sulfur-plugged valves caused the automatic H_2S product flow control to malfunction. Because of this, the H_2S production had to be controlled by manually changing the natural gas and steam feed rates.

After achieving reliable operation with a two-stage reaction, the bypasses, indicated in figure 3 removing reactor 2 from the system, allowed the entire reaction to take place in reactor 1 according to equation 4. This operation proceeded without problems; the only noticeable difference was that the product H_2S contained more COS and CH_4 .

Based on the initial Bureau of Mines laboratory work on H_2S generation, two other modes of operation were tried. During one-stage operation, the steam superheater was eliminated and steam was superheated together with the natural gas. This operation also proceeded without problems. Next, both the steam and natural gas superheaters were eliminated, and all reactant feed materials were superheated in the sulfur superheater. Again the plant worked satisfactorily; the only noticeable difference was that the temperature of the superheater could be reduced about 100°F without affecting the H_2S product quality. The advantages of such single-stage operation would be the elimination of capital equipment.

Between April and November 1975, the H_2S generator operated for more than 2,400 hours and provided the H_2S required for SO_2 reduction in the citrate process. During the latter 1,600 hours of this time, the single-stage reactor was used.

Table 3 summarizes results of the H_2S generator operation under reasonably steady-state continuous operation. During this time sulfur was fed to the H_2S generator while varying the natural gas and steam flows to change the H_2S production rate. Throughout most of the H_2S generator operation, the sulfur flow was about 160 pounds per hour. This flow provided between 150 and 300 percent excess sulfur, which was recovered and recycled. The large amount of excess sulfur was used to prevent overheating of the sulfur vaporizer coil and to transfer heat to the first reactor. During two-stage operation, a 25-percent excess of steam was used to prevent COS formation. During one-stage operation, where the CS_2 hydrolysis occurs at a higher temperature, a 50-percent excess of steam was necessary to achieve low COS in the product gas. The first reactor inlet and outlet temperatures both averaged about 566°C ($1,050^\circ\text{F}$). While operating with two stages, the second reactor inlet and outlet temperatures averaged 221°C (430°F) and 346°C (655°F), respectively. In addition to the principal gas analyses listed in table 3, the H_2S product gas contained about 1 percent N_2 and traces of CS_2 , CO , and O_2 .

TABLE 3. - H₂S generation results of The Bunker Hill
pilot plant operation, April-November 1975

Reactor stages	Number of super-heaters	Natural gas flow, lb/hr	H ₂ S production, ton/day	H ₂ S product analysis, vol-pct			
				H ₂ S	CO ₂	COS	CH ₄
2	3	12.2	1.15	79	19	0.7	0.4
2	3	8.1	.75	79	19	.5	.2
2	3	6.0	.55	79	19	.3	.2
1	3	10	.95	78	18	1.5	2.0
1	2	9	.85	77	17	2.4	2.1
1	1	7	.65	78	18	1.6	1.0

The test results show that the two-stage operation of the pilot plant makes the most efficient use of natural gas and produces the least amount of the impurity COS. The decrease in CH₄ utilization during one-stage operation, as indicated by the higher CH₄ in the product gas, may be caused by the increased space velocity through the first reactor. The increased COS content of the product gas formed during one-stage operation may result because the formation of COS is favored at higher temperatures. The COS in the H₂S product gas would be vented from the sulfur precipitation reactors, incinerated to SO₂ and CO₂, and returned to SO₂ absorption. By all methods of operation, the H₂S generator produced a gas which analyzed between 77 and 79 percent H₂S and was suitable for the SO₂ reduction reaction.

The quantities of sulfur, CH₄, and steam required for the H₂S generator for each short ton of H₂S produced were

1. Sulfur, 1,900 pounds
2. CH₄, 5,600 standard cubic feet
3. Steam, 1,000 pounds

These quantities assume that the H₂S product gas contains 1 percent COS and 0.5 percent CH₄ and that a 50-percent steam excess is necessary for the most efficient H₂S generation reaction.

To test SO₂ reduction with lower grade H₂S, such as would be made by using a CO-H₂ mixture from coal gasification in the manufacture of H₂S, the generator operation was modified to yield such a low-grade gas. By operating at a reactor inlet temperature of only 482° C, unreacted methane was increased, thus diluting the H₂S in the final product gas. This gas in the pilot plant proved suitable for SO₂ reduction and contained, in volume-percent on a dry basis, 56 H₂S, 15 CO₂, 24 CH₄, 1 COS, 0.5 CS₂, 2 N₂, and trace CO and O₂.

In general, the H₂S generator worked reasonably well after initial shakedown problems were eliminated. With additional refinements it would be able to produce suitable H₂S at a rate to match the normal requirements of the citrate process. However, corrosion and plugging of lines may be a continuing maintenance problem, even though probably reduced in a larger scale operation.

PROCESS DEVELOPMENT

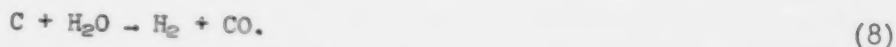
Research continues at the Salt Lake City Metallurgy Research Center to develop and improve the buffered SO₂-H₂S (citrate) process for removing SO₂ from industrial

stack gases. Two areas of this process development research that look encouraging are (1) H_2S generation using high-sulfur coal or coke in place of natural gas as a source of reductant, and (2) steam stripping of loaded solution as an alternative to sulfur precipitation by H_2S to produce strong SO_2 gas for feed to a sulfuric acid plant.

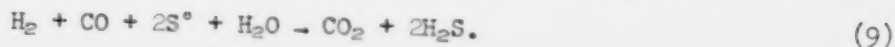
H_2S Generation Using Petroleum Coke

Research was initiated to investigate generation of H_2S for the buffered SO_2 - H_2S process by reacting a 5-percent-sulfur petroleum coke with steam and citrate-produced sulfur. The manufacture of H_2S from this raw material, typical of high-sulfur coke produced at oil refineries, would eliminate the dependence of the citrate process on natural gas. Utilization of this high-sulfur petroleum coke, which cannot be burned in many areas because of air-pollution standards, would help in solving some of the stockpiling problems presently developing at many oil refineries.

Initial research was directed toward a two-stage procedure whereby the coke was first reacted with steam in a vertical tube furnace at 800° to 900° C to produce a water gas containing predominately hydrogen (H_2) and CO according to the following reaction:



The water gas was then reacted with vaporized sulfur and more steam in a horizontal tube reactor where H_2S and CO_2 were produced by the following reaction:



In the best test to date, reaction of the sulfur-bearing coke and steam at 860° C ($1,580^\circ$ F) resulted in a gas containing, in volume-percent on a dry basis, 52 H_2 , 42 CO, 4 CO_2 , 2 H_2S , and a trace of CH_4 . Reaction of this gas with sulfur vapor and more steam over an alumina catalyst at 550° C ($1,020^\circ$ F) produced a gas containing, in volume-percent on a dry basis, 68 H_2S , 31 CO_2 , and the remainder CO, COS, and CH_4 . Such a gas would be suitable for precipitation of elemental sulfur and regeneration of absorbent liquor in the citrate process.

Steam Stripping

Investigations have been continued to determine the feasibility of utilizing steam stripping in the buffered SO_2 - H_2S process as an alternative to H_2S stripping for removing SO_2 and regenerating the absorbent liquor. Strong SO_2 gas would be recovered as an end product in place of elemental sulfur. Such a procedure might be applicable where markets exist for SO_2 or H_2SO_4 , or where acid plant tail gas could be reduced to acceptable levels by the citrate process and the strong SO_2 gas produced could be recycled to the acid plant feed gas stream.

Continuous tests have been initiated in a bench-scale, integrated absorption-stripping apparatus to treat gases containing 0.25 and 0.5 percent SO_2 . This covers the SO_2 concentration range normally found in acid plant tail gas. Absorption of SO_2 is carried out at 45° to 50° C using a 0.5 M citrate solution at pH 4. The steam stripping column is operated at 94° C. Preliminary tests indicated high steam consumption, but better results are being obtained with heat losses in the system reduced by added insulation, near-isothermal conditions maintained in absorption and stripping columns, and improved utilization of the steam.

In the best test to date, 95 percent of the SO_2 was removed from feed gas, using about 12 pounds of steam per pound of SO_2 recovered. Sodium thiosulfate is added to the citrate solution to inhibit oxidation of SO_2 to $\text{SO}_4^{=}$. To date, SO_2 oxidation in the system has been about 1.3 percent, which is comparable with the oxidation rate obtained when H_2S is used for regeneration of citrate solutions.

The results of Bureau investigations indicate that steam stripping might be an alternative to H_2S regeneration in the citrate process when extremely high absorption is not needed and inexpensive steam is available.

DEMONSTRATION PLANTS

Plans are underway for construction of a large-scale plant to demonstrate the applicability of the citrate process for SO_2 emission control at powerplants burning high-sulfur coal. The demonstration plant would operate on a 50- to 100-MW powerplant, and would be constructed and operated under a cooperative arrangement and cost-sharing basis between the Bureau of Mines, the Environmental Protection Agency, and interested industrial firms.

Work on the citrate demonstration plant will be divided into four phases. Phase I, consisting of process design and definitive cost estimates, should be completed by the end of 1976. Phase II, which includes detailed engineering design, construction, and mechanical acceptance of the plants, should be completed by the end of 1979. Phase III, consisting of startup and performance acceptance testing, would take place at the conclusion of Phase II and would be followed by Phase IV, which consists of comprehensive emission testing programs to be conducted at the demonstration plant by independent contractors for 1 year.

COST ESTIMATE FOR CITRATE PLANT AT COAL-BURNING POWERPLANT

Based on results of the Bunker Hill pilot plant operation, the Process Evaluation Group at the Salt Lake City Metallurgy Research Center estimated capital and operating costs for the treatment of flue gas from a 1,000-MW coal-burning powerplant. This would include fly ash removal in an electrostatic precipitator followed by removal of 95 percent of the contained sulfur. The powerplant was assumed to operate 7,000 hours (292 days per year) and to burn 8,400 tons per day of coal containing 3 percent S; the gas flow would be 1,730,000 scfm (60° F) with an SO_2 content of 0.24 percent. Under these conditions, the yield of sulfur would be about 214 long tons per day or 62,344 tons per year.

Annual operating costs for the plant are itemized in table 4. A summary of operating labor requirements, fixed capital costs, annual operating costs, and unit production costs for each of the unit operations and for the entire plant is presented in table 5. The fixed capital costs were estimated by standard chemical engineering cost estimating procedures for a "study estimate" and are for 1975 or a Marshall and Swift (M&S) index of 453.

TABLE 4. - Annual operating cost of SO₂ removal from
1,000-MW powerplant offgas

	Operating cost	Total cost
Direct cost:		
Raw materials:		
Citric acid	\$593,000	
Soda ash	206,000	
Kerosine	486,800	
Lime	<u>22,600</u>	
		\$1,308,400
Utilities:		
Electricity	399,500	
Natural gas	2,346,900	
Process water	52,600	
Cooling water	221,300	
Steam	<u>2,731,900</u>	
		5,752,200
Direct labor:		
Labor	237,200	
Supervision	<u>35,400</u>	
		272,600
Plant maintenance:		
Labor	1,127,000	
Supervision	225,400	
Materials	<u>1,305,200</u>	
		2,657,600
Payroll overhead	-	406,300
Operating supplies	-	<u>531,500</u>
Total direct cost		10,928,600
Indirect cost (administration and overhead)		1,384,700
Total capital charges		<u>14,461,700</u>
Total annual operating cost		26,775,000

TABLE 5. - Summary of costs for SO₂ removal from a
1,000-MW powerplant offgas

	Number of operators	Capital cost	Annual operating cost	Unit production cost per long ton of sulfur
Electrostatic precipitator	2.0	\$21,564,600	\$4,208,500	\$68
Gas cooling	2.0	11,546,700	4,813,600	77
SO ₂ absorption	4.2	14,159,900	6,288,400	101
Sulfur precipitation	2.1	1,013,700	2,275,300	36
Sulfur recovery	2.1	3,249,500	2,220,000	36
H ₂ S generation	4.3	12,685,700	6,690,200	107
Na ₂ SO ₄ removal	2.3	598,200	279,000	5
Facilities	-	6,464,100	-	-
Utilities	-	7,756,600	-	-
Total fixed capital	-	79,039,000	-	-
Working capital	-	5,722,000	-	-
Total	19.0	84,761,000	26,775,000	430

The operating cost of the citrate plant includes reheating the final tail gas from 50° to 77° C (122° to 170° F) with a natural gas burner at the base of the power-plant stack, and the neutralization of liquid effluents with lime. Operating losses are assumed at 19 pounds of citric acid and 12 gallons of kerosine per long ton of product sulfur. Costs for Na₂SO₄ removal were estimated on the basis of 1.5 percent of the removed sulfur being converted to sulfate.

Direct costs include materials and utilities at the following unit costs: Citric acid at \$1,000 per ton, soda ash at \$60 per ton, kerosine at \$0.65 per gallon, lime at \$35 per ton, electric power at \$0.01 per kW-hr, natural gas at \$1.00 per thousand cubic feet, water at \$0.17 per thousand gallons for process use and \$0.03 per thousand gallons for cooling, and steam at \$1.00 per thousand pounds. These costs also include direct labor at \$6.00 per hour, plus supervision at 15 percent of direct labor; plant maintenance consisting of maintenance labor at 1.5 percent of fixed capital costs, plus supervision at 20 percent of maintenance labor, and maintenance material at 116 percent of maintenance labor; payroll overhead at 25 percent of the cost of labor and supervision for operations and maintenance; and operating supplies at 20 percent of plant maintenance.

Indirect costs are 40 percent of direct labor, plant maintenance, and operating supplies.

Capital charges, which include amortization, taxes, and insurance, are 17 percent of the total capital, which is the average annual fixed capital charge for privately financed steam-electric plants.

As shown in table 5, the capital investment for a citrate plant including an electrostatic precipitator at a 1,000-MW coal-burning powerplant is estimated at \$84.8 million. Assuming no credit for sulfur, operating cost for removing 95 percent of the SO_2 from the stack gas is about \$26.8 million. This is equivalent to \$10.93 per short ton of coal or 3.8 mills per kW-hr.

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APCI/IFP RENERATIVE FGD AMMONIA SCRUBBING PROCESS

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ABSTRACT

A brief history of the utilization of ammonia for the absorption of SO_x is the preliminary to the introduction of specific technology developed by Air Products and Chemicals, and Institut Francais du Petrole. Their combined work has produced a fully regenerable second generation flue gas desulfurization process. Process chemistry and pilot plant activities are fully explored.

APCI/IFP REGENERATIVE FGD AMMONIA SCRUBBING PROCESS

The very rapid rate of chemical absorption of sulfur dioxide by ammonia has been known and to some extent applied for many years. Broad adoption of ammonia scrubbing has been inhibited by the production of a sub-micron particulate, which results in a characteristic, but environmentally unacceptable "blue plume." Key advances have been oriented towards fumeless ammonia scrubbing technology developed by Catalytic's parent organization, Air Products and Chemicals, Inc.⁽¹⁾

A combination of this technology with an existing liquid Claus process developed by Institut Francais du Petrole (IFP), the French research and process development organization, offers a true second generation stack gas scrubbing process. The ammonia absorbent is completely regenerated and recycled and the sulfur is recovered in its elemental form.

Initial ammonia SO₂ absorption dates back to 1883 when a British patent was issued to Ramsey⁽²⁾. Further, in the period of 1935 to 1952, Johnstone and co-workers developed basic data at the University of Illinois. Five major papers were published as a result, which dealt with absorption of SO₂ by ammoniacal solutions and desorption from the absorber effluent.^(3,4,5,6,7)

Abroad, considerable data were collected by Chertkov and his co-workers in Russia during the 1950s and are covered by over 40 papers on sulfur oxide recovery and ammonia absorption.

One of the oldest commercial applications of SO₂ ammoniacal absorption began in about 1936 by the Consolidated Mining and Smelting Company⁽⁸⁾ now Cominco Ltd., located in Trail, British Columbia. The unit removes SO_x from smelter waste gases. The system products are ammonium sulfate and SO₂. The unit is still operating today.

In Japan, the Showa Denko Company has operated a 25 MW equivalent ammonia absorption test unit on stack gases from an oil fired system yielding an ammonium sulfate byproduct.⁽⁹⁾

Processes similar to the unit still in operation at Cominco are in full scale operation on sulphuric acid plant tail gases in Czechoslovakia and Romania.^(10,11) These processes produce ammonium sulfate, which may have a limited market.

In this country, a number of sulfite paper processes presently utilize ammonia scrubbing on a 24-hour per day, seven day week basis without problems. Systems operate a scheduled 362 days per year and successfully reduce SO₂ concentrations in the range of 8,000 to 20,000 parts per million down to about 150 ppm without operating or reliability problems.

In order to adapt the acid plant tail gas ammonia scrubbing method to the power plant stack, TVA carried out pilot plant activities in 1953-54.⁽¹²⁾ It is apparent that demand for the ammonium sulfate byproduct severely limits use of this system in the United States.

In more recent TVA work, ammonia absorption processes yielding a fertilizer byproduct known as far back as the 1920s have been investigated at the Colbert Power Station facilities.

Program results⁽⁹⁾ indicated that the most severe problem of the ammonia absorption process was the formation of a dense, persistent plume. Removal of the plume by electrostatic precipitation was reported by TVA to be about 50% at superficial velocities of 15 feet per second.

Personnel from Southern Research Institute of Birmingham, Alabama, determined the fume mean particle size to be 0.25 micron with 10^7 particles/cm³ in the range of .005 to .5 micron.

Air Products, as a result of extensive studies, postulated a mechanism for solid particulate plume formation. Laboratory studies verified that the proposed mechanism was indeed the controlling system of plume formation. With the mechanism confirmed, Air Products' scientists were able to establish a set of criteria which fully define an envelope of operating conditions which largely or wholly prevent or eliminate the formation of an ammonia salt plume. These criteria are patented⁽¹⁾ and are the result of a rigorous theoretical and experimental program carried out by the Research and Development Department at Air Products.

Utilizing these established operating criteria, Air Products personnel were literally able to turn the plume on and off in a laboratory system by adjusting the operating parameters. During the period 16 April to 4 May, 1973, a test program was conducted at TVA's Colbert Station. These tests, sponsored jointly by TVA, EPA and Air Products/Catalytic, were conducted as a factorial series to explore the pluming characteristics of the system over a range of operating conditions in an insulated scrubbing tower. Run number I-14A, operating within the Air Products specified envelope of conditions, resulted in zero opacity as observed by two EPA certified plume readers.

TVA concluded in its report⁽⁹⁾ that "Plume formation while producing a liquor with high salt concentration ($CA > 12$) can be controlled by proper operation of the scrubber."

New technology providing for removal of SO₂ utilizing ammoniacal solutions without associated plume formation is the basis for our entry into this field.

Our licensing agreement with Institut Francais du Petrole allows us to combine our ammonia scrubbing technology with a process to convert the spent ammoniacal brine to elemental sulfur^(13,14,15,16,17) with essentially full recovery of ammonia values for recycle.

At present, Catalytic is operating a 2 MW ammonia scrubbing system at Calvert City, Kentucky. It is fed a gas slip-stream from two 20 MW equivalent coal-fired industrial boilers firing 3.2% sulfur coal. Startup of the unit was early February.

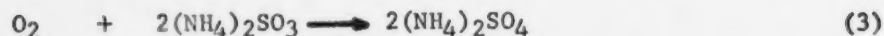
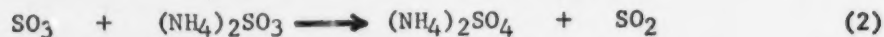
Concurrently, IFP is running their recovery process on a 30 MW scale at the Electricite du France at Champagne. The unit produces a bright yellow sulfur.

I. THE CHEMISTRY

Air Products and Chemicals has developed a special cycle synthesis computer program which enables the user to establish a material and energy balance consistent with a given set of conditions for the absorption process. The program also checks these operating conditions against the plume avoidance criteria.

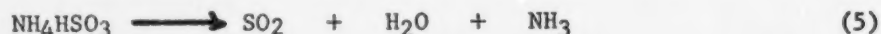
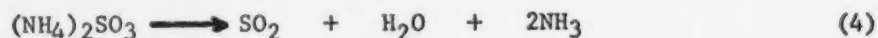
In a typical 3-1/2% sulfur coal case, four stages of SO₂ absorption are employed to effect 90% removal. Each stage is fed fresh ammonia makeup while brine leaving the stage is split between the downcomer and a stage recirculation loop. Control of the process is effected by automatic pH controlled addition of fresh ammonia to each stage.

The principal absorption reactions are as shown here:

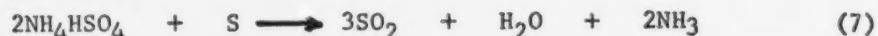
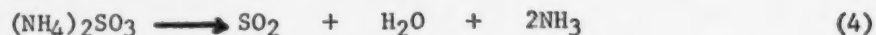


The formation of ammonium sulfate is inevitable with absorbent in contact with SO_3 and oxygen. Sulfates are readily converted in the recovery process.

Spent brine from the absorber is first processed in a forced circulation evaporator where about seventy percent of the stream is reduced to SO_2 , H_2O , and ammonia as shown by these equations:



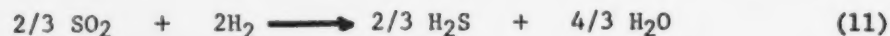
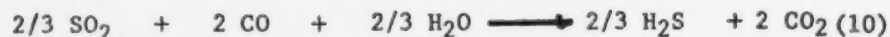
The balance of the stream which contains the sulfate load plus remaining sulfite is converted in the sulfate reducer along with a slipstream of elemental sulfur to ammonia, SO_2 , and water as follows:



A small amount of SO_3 exits with the converted stream which passes through a catalytic bed where it is converted directly to SO_2 as shown:

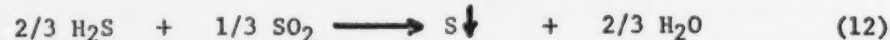


All vapor streams are combined and next pass to the hydrogen sulfide generator. Here two thirds of the SO_2 is converted to H_2S by the following catalyzed reactions:



The reaction proceeds with either CO or H_2 as a reducing agent.

The stream containing H_2S and SO_2 enters the liquid Claus reactor where elemental sulfur is produced as a result of the following reaction:



Finally, the gas stream leaving the liquid Claus is treated to recover the ammonia values and concentrate them for return to the absorber. The non-condensable gas stream is vented to the boiler combustion inlet air or incinerated.

II. THE PROCESS

Now that we have reviewed some of the process background and chemistry, let us take a look at a typical process schematic which is depicted in Figure 1.

Battery limits begin at the exit flange of the electrostatic precipitator. The process begins with a blower of sufficient power to drive the gas through gas conditioning and SO₂ absorption steps and finally out the stack.

Although we normally think in terms of a forced draft fan in the dry position for a typical application, flue gas composition, especially particulate loading, can affect this approach.

Gas enters a low pressure drop venturi at about 300°F. When the gas is brought in contact with the recirculating water, it is brought to its adiabatic saturation temperature of approximately 125°F. Contact time is a fraction of a second. During the turbulent liquid to gas contact, over 90% of the chlorides and about half of the SO₃ are absorbed in the recirculating liquid in which the pH is maintained at about two. The composition of the recirculating venturi liquid is the basis for control of the purge stream from the system. The purge is utilized to maintain chlorides below 5,000 ppm and/or total dissolved solids below 5%. For a typical 500 megawatt case, it is estimated that purge stream from the humidifier would be approximately 5 gpm. It would be discharged directly into the utility plant's fly ash pond where its acidic components would help to neutralize the alkaline fly ash discharge.

From the flue gas composition and its thermodynamic characteristics, operating conditions can be set that result in fumeless operation of the absorber. It is then simply a matter of maintaining these conditions for each stage such that expected system perturbations do not carry the absorption process into the fuming regime. An envelope of operating conditions is maintained to assure that expected variations in temperature and SO₂ concentrations do not cause a plume to form.

Presently, a valve tray absorber configuration is utilized in the design. We consider it a very desirable initial approach due to the extensive technical data that exist for such designs. A typical four-tray system is expected to induce about a 12" water pressure drop. Catalytic anticipates extending its technology into less energy demanding absorber configurations.

The Catalytic/Air Products approach to plume avoidance comprises stage-wise control of temperature and composition. In its capability as engineer/constructor, Catalytic has designed and erected many chemical plants whose process control requirements were far more sensitive and demanded greater sophistication than the SO₂ absorption step. We view control of the ammonia system as a routine process operation. Liquid phase pH and density have been related directly to composition, providing the determinant relationship for liquid phase control.

Ultimately, spent liquor exits the absorber from the bottom stage where it is held in storage or sent directly to the IFP recovery process. It is most practical to operate the recovery section at a constant liquid load, and for this reason, interprocess storage becomes desirable.

The recovery section need not be situated in close proximity to the absorption section. Use of spent brine and regenerated ammonia storage tankage permits location of the recovery (IFP) process unit on a distant plot connected only by spent and fresh liquid absorbent lines.

APCI-IFP
REGENERATIVE FGD PROCESS
SCHEMATIC

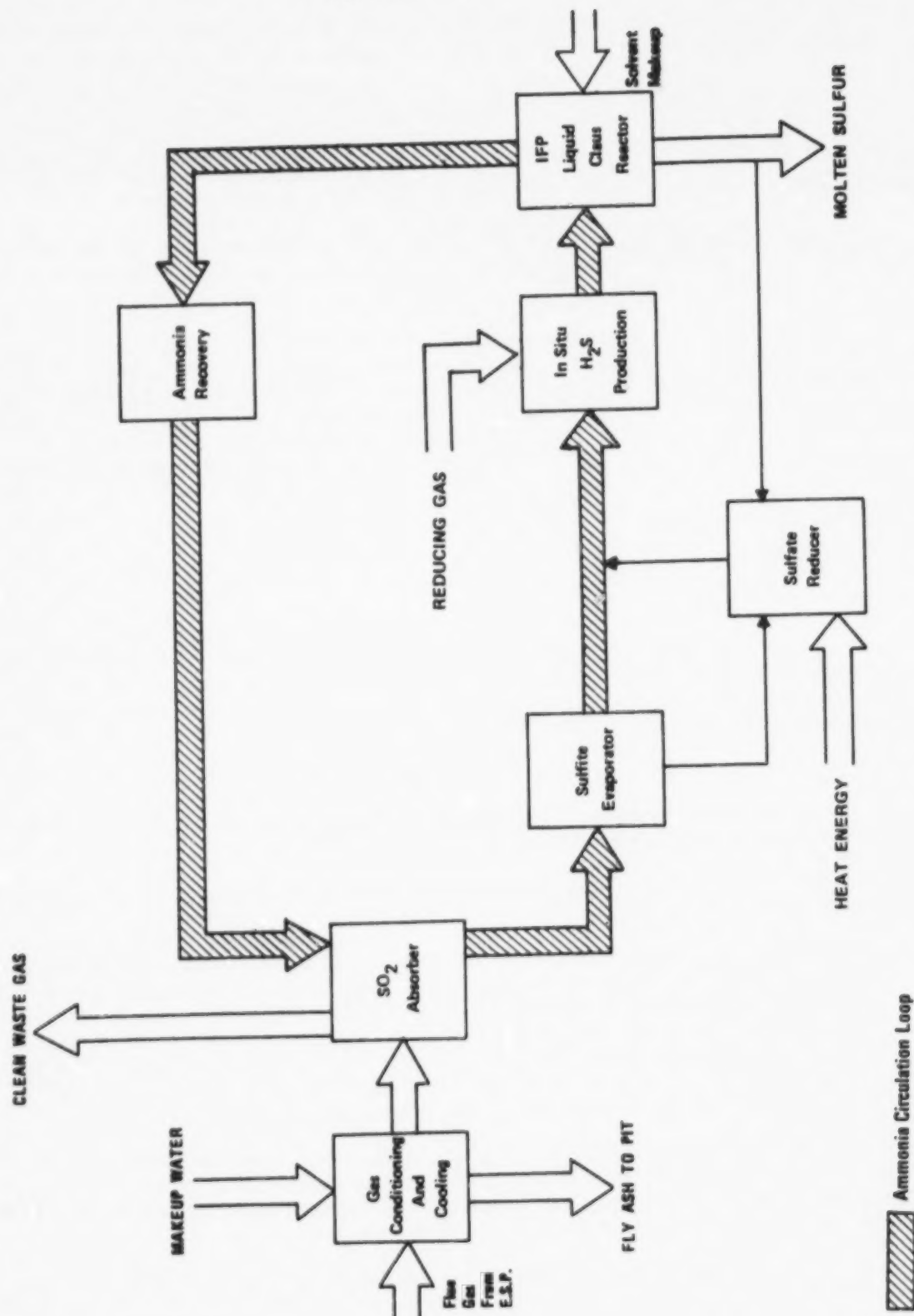


Figure 1.

Spent ammoniacal brine is fed at a constant rate from the storage tankage through a filter to a forced circulation evaporator where sulfite decomposition occurs. The process is driven by low pressure steam derived almost completely from another step in the process.

Sulfates are combined with a slipstream of molten sulfur and reduced in a submerged combustor. In this unit, a gas is burned with about 95% of the stoichiometric air requirement. The exhaust gases are brought in direct contact with the bath of ammonium sulfate, sulfite, and sulfur. The bath is maintained at approximately 700°F.

The exit gas contains H_2O , SO_2 , NH_3 and trace SO_3 which is reduced to SO_2 in a catalytic converter.

There are non-volatile impurities which collect in the sulfate reducer. These are purged on an intermittent as-required basis. The waste stream purged from the reducer is small in quantity and can be sold as fertilizer. If inappropriate, the sulfate waste could be wet with water and sprayed on the power station's coal pile for combustion with the coal. The ammonia has some heat value and decomposes at firebox temperatures. The sulfate will reappear as SO_2 .

The SO_2 rich gas stream is then united with reducing gas and allowed to combine to form H_2S in a special catalytic reduction reactor. The effluent gas stream contains an approximate 2/1 mole ratio of H_2S to SO_2 . This reaction is highly exothermic with the exit gas temperature reaching about 900°F. The flow from the catalytic reducer enters a waste heat boiler and leaves at about 320°F, ready for the liquid Claus step. The waste heat is removed as low pressure steam which is utilized for sulfite evaporation.

Gases at about 320°F pass into the liquid Claus unit. It is here that the SO_2 and H_2S combine to form elemental sulfur. The molten product is taken off the bottom of the unit while the ammonia, water vapor, nitrogen, CO_2 , and trace amounts of other combustion gases flow out the top. Recovery of the ammonia values is accomplished by absorption, and distillation enriches the concentration to usable levels.

From here, the ammonia is recycled to the fresh absorbent storage tank, thereby closing the loop. Non-condensables are either catalytically incinerated or discharged to the combustion air inlet of the boiler.

It is proposed that an air blown gasifier be employed to supply heat for sulfate reduction and low btu reducing gas for the H_2S generation step. The CO values in reducing gas are used with equal ease as the hydrogen values for the H_2S production step prior to sulfur make in the liquid Claus. When coal is fired in the gasifier, the hot producer gas would enter a cleanup system to remove tars, fly ash and carbon fines by condensation, scrubbing, and electrostatic precipitation.

Ammonia and SO_2 that pass through to the process are not a problem since both already exist in large quantity and they have no upsetting effect on the material balance. The process can utilize both the H_2 and CO values of the gas. It is envisioned that a gas holder would be installed between the gasifier and the process.

Excluding all contingencies and assuming the coal charge to the gasifier to be considered a raw material, we envision an approximate 2.8% of the power plant capacity as an electrical requirement and an additional 1.6% as steam for a total of 4.4% of the power plant output. This includes steam to provide reheat of 50°F. This represents the steady state energy requirement for the process.

III. APPLICATIONS

Figure 2 shows the 4" diameter glass bench scale scrubber in Air Products' Allentown, Pennsylvania laboratories which was used to develop data and to confirm results of the theoretical and experimental studies on which the process is based.

Figure 3 shows our 2 MW pilot facility which is dedicated to the optimization of the SO₂ absorption step. The system has been fabricated on two transportable skids. One contains the blower, cooler, and absorber, while on the second we have located the interstage pumps and associated tankage, with the control house package making up the third. We intend to gain hard data required for engineering design of commercial systems as well as look into alternate control systems. In the not too distant future, we hope to be in a position to offer the unit for demonstration purposes to potential customers.

IFP has a 30 MW demonstration of its recovery process in Champagne, at Electricite de France. Most of the unit operations are vertically stacked for a minimum land area requirement. The system utilizes a slipstream from a 200 MW oil-fired boiler. The ammonia scrubber uses European technology and does plume; however, the exhaust is co-mingled with the boiler effluent.

In conclusion, the ammonia process has a long history of reliable applications, both in the United States and abroad. At present, the opacity emission regulations have reduced its potential for use without considerable additional capital and operating cost to eliminate the plume once formed. Utilizing the technology discussed here today, we think that the ammonia process is a reliable and viable method for SO₂ removal with complete regenerative capability yielding elemental sulfur. The overall process is reliable in operation, avoids the obvious scaling problems by virtue of using a clear liquor scrub, does not require constant replacement of absorbent and catalysts, produces a salable sulfur and does not generate environmentally objectionable by-products. It can use a reducing gas obtainable from currently available coal gasifiers, using coal from the plant supply. Finally, it is attractively cost competitive with all second generation processes and first generation approaches, particularly in large sizes.

Figure 2. APCI 4" Diameter, 4 Stage,
Glass Bench Scale Ammonia
Absorber

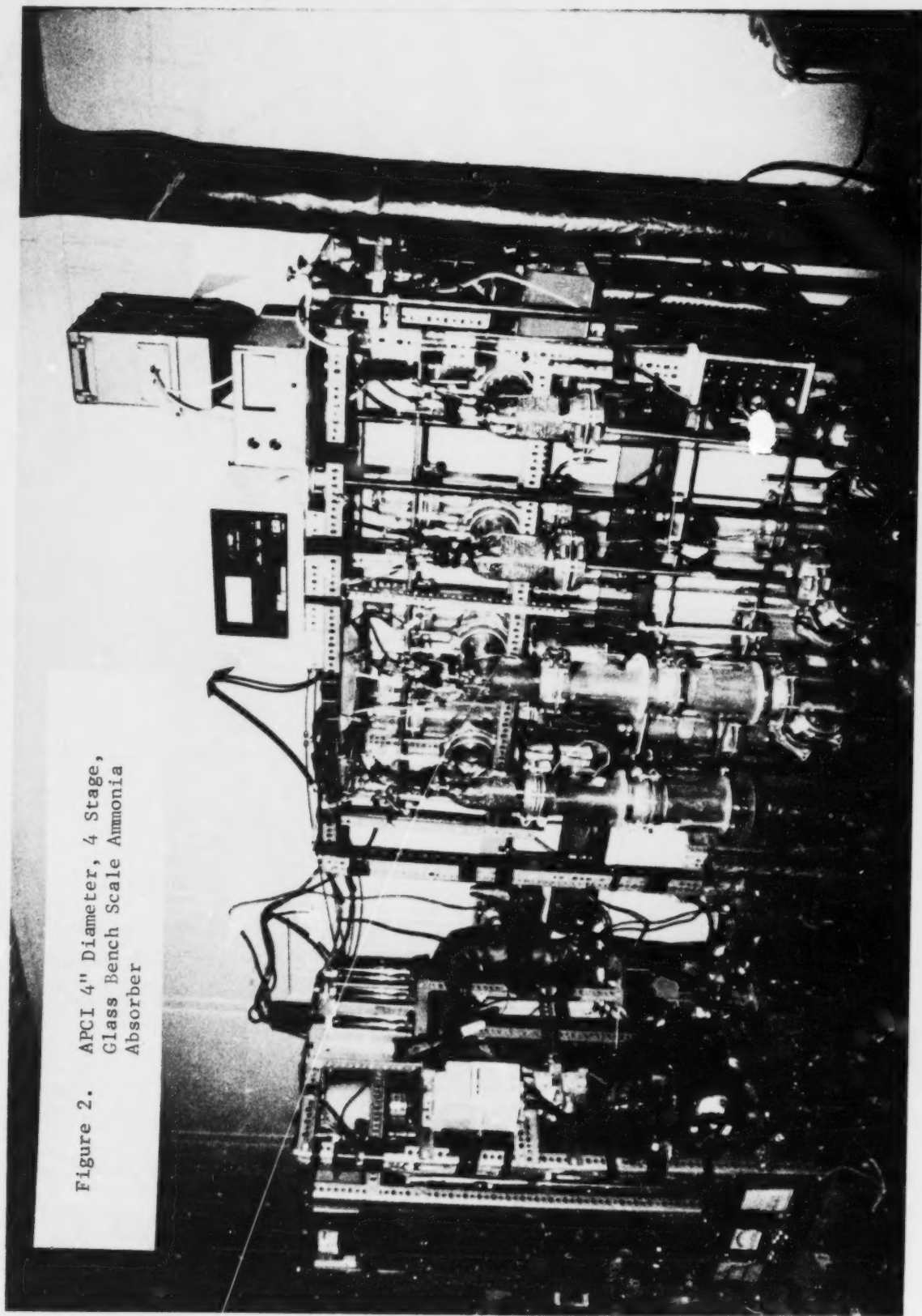


Figure 3. 2 MW Ammonia Absorption
Pilot Plant Located in
Calvert City, Kentucky



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BF DRY ADSORPTION SYSTEM

PART I

FW-BF Gulf Power Demonstration Unit Interim Results

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PART II

BF-STEAG Demonstration Unit Operational Experience and Performance

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ABSTRACT

This process uses activated char to remove SO_2 and particulate matter from boiler flue gas. The char is thermally regenerated and the SO_2 rich gas is converted to elemental sulfur.

PART I of the paper presents interim results of the FW-BF Dry adsorption System installed as a demonstration unit at the Scholz Steam Plant of Gulf Power Company in Sneads, Florida. Current status, operating experiences and plans for the future of the process are reviewed.

PART II of this paper presents the operational experience and performance of the Bergbau-Forschung SO₂ Removal System installed as a demonstration unit at the Kellerman Power Station of STEAG in Lunen, West Germany. The results of extensive operation of the adsorption, regeneration and sulfur reduction sections are presented and the flexibility of the unit to cycle successfully in response to peaking operation is described.

PART I
GULF POWER DEMONSTRATION UNIT
Interim Results

I. Introduction

A 20 MW demonstration dry adsorption system was put into operation at the Scholz Steam Plant of Gulf Power Company near Sneads, Florida, Figures 1 & 2. This system is one of three advanced flue gas desulfurization units of 20 MW size installed at the plant as part of a technology evaluation program being conducted by Southern Services, Incorporated, for the Southern Company. The Southern Company is an electric utility holding company including Alabama Power Company, Georgia Power Company, Gulf Power Company, Mississippi Power Company, Southern Electric Generating Company and Southern Services, Incorporated. The general design conditions for the unit are shown in Table I.

TABLE I
Summary of General Design Conditions

Unit Rating - Adsorption Section	20 MW Nominal
Unit Rating - Regeneration & RESOX* Sections	40 MW Nominal
Coal	
HHV	12,400 BTU/#
%S	3
% Ash	14
Flue Gas	
Quantity - #/Hr.	278,940
Temperature - °F	326

*Trademark of Foster Wheeler Energy Corporation

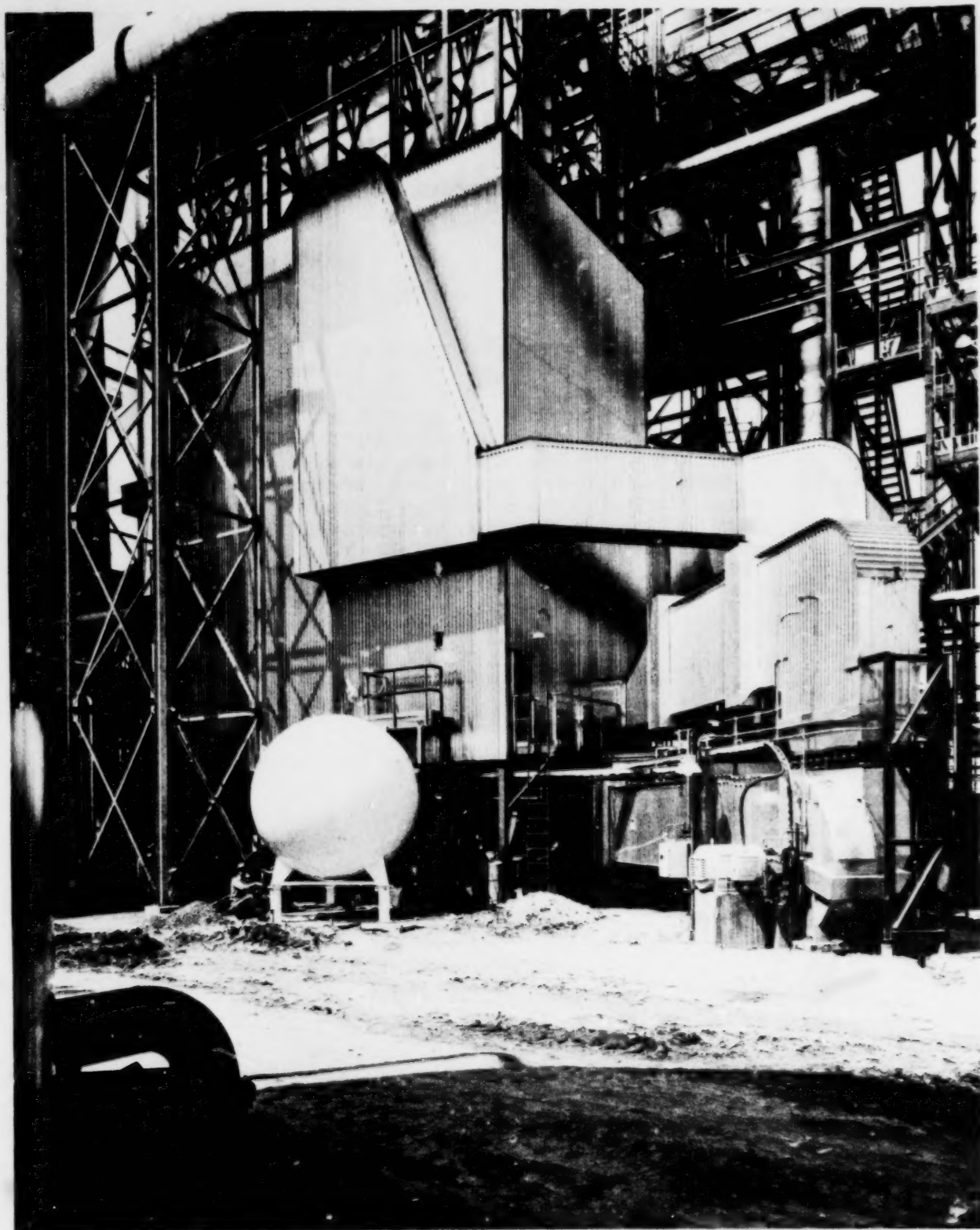


Figure 1: Adsorption Section - Gulf Power Company

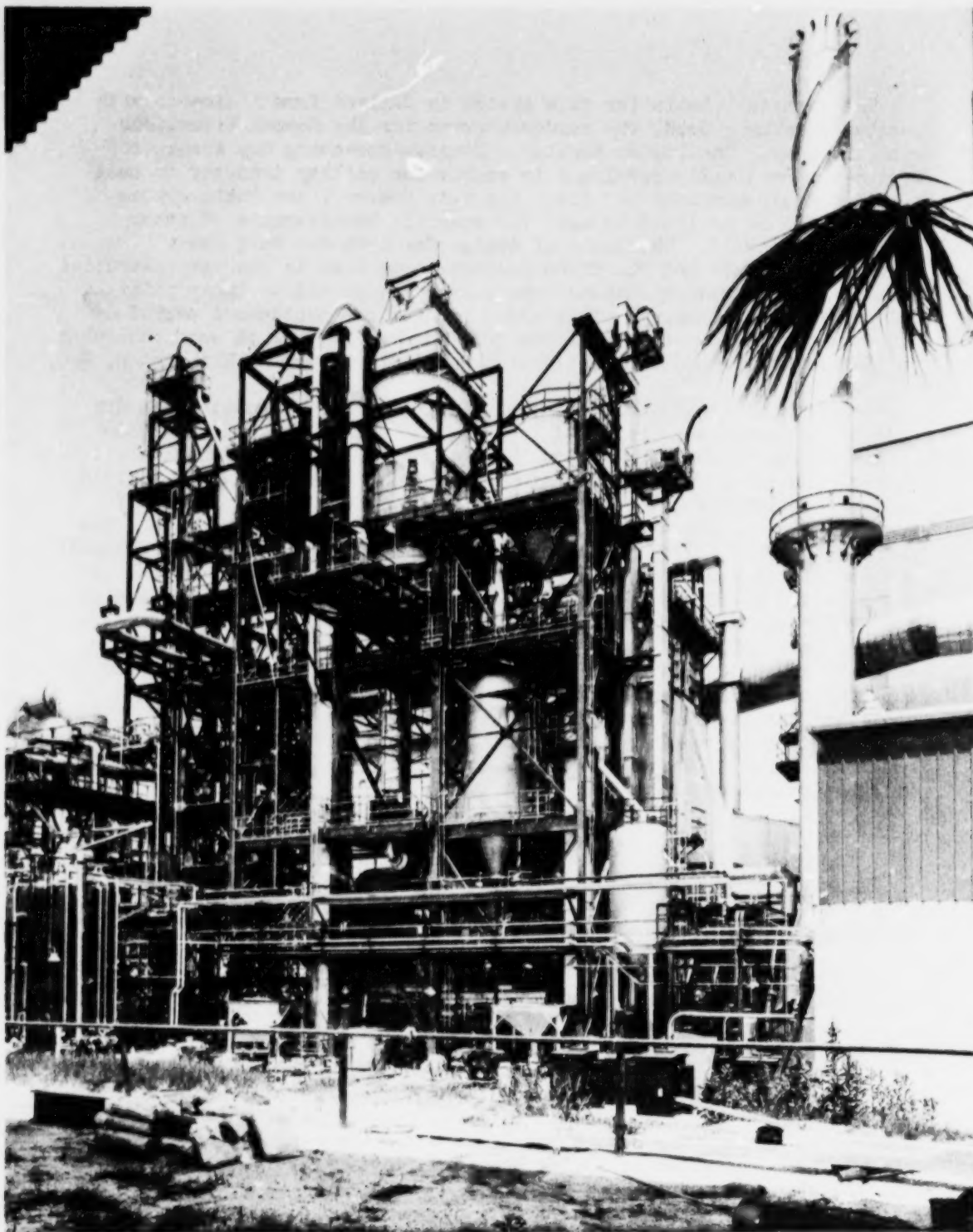


Figure 2: Regeneration and Resox* Sections - Gulf Power Company

The technical basis for this system is derived from a license with Bergbau-Forschung GmbH, the research group for the German Bituminous coal industry. The Foster Wheeler - Bergbau-Forschung Dry Adsorption System was originally developed to enable the utility industry to meet certain requirements of the Clean Air Act; however, the basic system can and will be utilized to meet the specific requirements of other industries as well. The basis of design for both the Gulf Power Demonstration Unit and the STEAG Demonstration Unit is the very extensive work done by Bergbau-Forschung over a two year period at their pilot unit at Welheim, Germany. This plant ran for one continuous period of 6,000 hours and the results of the two year testing period were published in 1970 at the Second International Clean Air Congress in Washington, D.C.

The initial construction of the Gulf Power 20 MW demonstration dry adsorption system was completed in May, 1975 followed by a three month commissioning (shakedown) period. The Adsorption and Regeneration sections initial shakedown run with passage of flue gas began on August 11, 1975 and was continued for a period of 10 days. During the later part of October, 1975 sections of the FW-BF system were run for five days. The purpose for this activity was to conduct an operational run on the RESOX* portion of the system at full operating temperatures and on process off-gas from the FW-BF front end subsystem. The delay between shakedown of the RESOX* section and the remainder of the system was caused by a lag in the construction of the two plus the need for pre-startup modifications to the RESOX* start-up heater. This paper covers the operating experiences during these initial shakedown runs, the subsequent modifications program and pre-startup testing. In early February, 1976 a formal test program was initiated by Southern Services, Incorporated and Foster Wheeler Energy Corporation. The results of this test program will be published in the future.

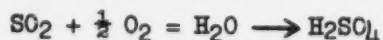
II. FW-BF Dry Adsorption System

A. Process Chemistry

The process chemistry of the FW-BF Dry Adsorption System for the Adsorption, Regeneration and RESOX* sections are described below.

Adsorption

Boiler flue gases containing SO₂, NO_x, oxygen, water vapor and particulate matter come into contact with the char pellets, which are the adsorption media. The SO₂, oxygen, and water vapor are adsorbed onto the char. The combination of moving char and flowing flue gas give rise to the following reaction:



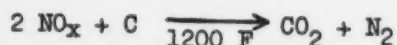
The char activity acts as a catalyst in this reaction. In addition SO_3 and nitrous oxides are similarly adsorbed. While it is easily understood how SO_3 is adsorbed, the principles of the adsorption of nitrous oxides are still under extensive investigation both in Germany and here in the United States. Particulate matter is collected on the surface of the char pellets which act as an impingement filter due to their size and physical arrangement.

Regeneration of the Adsorbent

When the activated char containing sulfuric acid is heated over 1200 F it undergoes the following reaction:



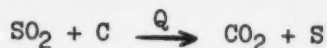
The nitrous oxides adsorbed are reduced according to the reaction:



These reactions result in the production of a concentrated and reduced volume stream of off-gases consisting of SO_2 , CO_2 , H_2O , and N_2 . The SO_2 concentration of this stream is in a range of 25 to 40 percent by weight. Particulate matter is physically separated from the saturated char prior to regeneration.

RESOX (Reduction of Sulfur Dioxide by Coal)

The concentrated off-gases produced in the Regeneration Section are introduced in counterflow to a mass flow of crushed anthracite coal. The reactions occurring in the reactor can be reduced to the simplified equation:

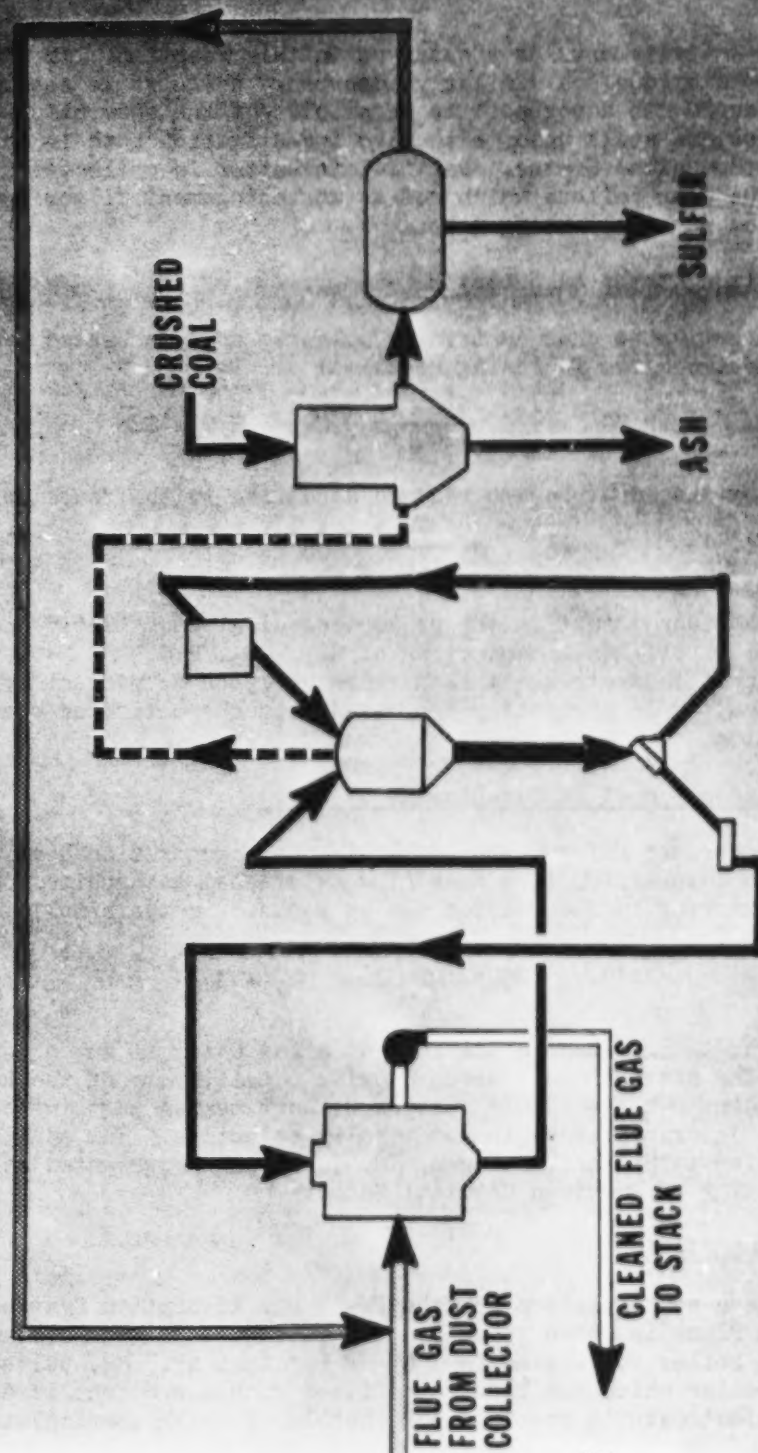


The sulfur is produced in the form of a gas which is subsequently condensed. The nitrogen and carbon dioxide constituents of the Regenerator off-gas pass through the RESOX* reactor without taking part in the reactions. The reaction described above is not totally selective. For additional information refer to Steiner, Juntgen, Knoblauch paper presented at 167th National Meeting of American Chemical Society.

B. System Description

The process configuration for the FW-BF Dry Adsorption System at the Scholz Steam Plant is shown schematically in Figure 3. The system is installed on Boiler No. 2 a nominal 40 MW (maximum 47.5 MW) pulverized coal-fired boiler which has been retrofitted with a sectionalized, high efficiency electrostatic precipitator capable of 99.7% particulate removal.

FW-BF SYSTEM



ADSORPTION

REGENERATION

RESOX*

* A TRADEMARK OF FOSTER WHEELER CORPORATION

Figure 3

FW-176-015

The FW-BF Dry Adsorption System is sized to handle one-half of the total flue gas from this boiler. The 20 MW equivalent in flue gas entering the system is 85,600 ACFM. The flue gas leaving the boiler air pre-heater is at a maximum of 350 F. The system is nominally designed to meet Florida SO₂ reduction codes of 1.2 # SO₂/MMBTU heat input which equates to a 74.5% removal efficiency requirement for 3 percent sulfur, 12,200 BTU/# fuel. The actual performance of the unit during initial operation far exceeded this requirement. Further testing during the formal test program will determine the limits of SO₂ removal as well as those of NO_x and particulate removal. These test program results will be the subject of future papers.

The operation of the FW-BF Dry Adsorption System can be conveniently broken down into three major sections: Adsorption; Regeneration; and RESOX*. The equipment utilization and operation of each of these sections is discussed as follows:

1. Adsorption Section

The adsorber is the key to the system. Adsorption is accomplished by passing the flue gas horizontally through vertical columns of activated char in the adsorber.

The Gulf Power Demonstration Unit adsorber consists of 2 vertical stages of char beds designed in a modular fashion. There are eight 6' x 6' beds in the 1st stage and four 4' x 4' beds in the 2nd stage. All beds are approximately 40 feet high.

The char in the beds is continuously recycled. A conveyor at the top of the adsorber feeds regenerated char into a holding tank which has discharge tubes that gravity feed the regenerated char into the individual char beds. The char moves downward in mass flow adsorbing SO₂ and NO_x as it travels. The char flow rate is controlled by a vibromagnetic feeder at the hopper outlet below each char bed. The saturated char is collected at the discharge of these feeders and sent by a combination of natural frequency conveyors and bucket elevators to the Regeneration Section of the system.

The flue gas entering the adsorber is tempered, if necessary, by the use of a dilution air fan (vane axial type) which maintains an inlet flue gas temperature of approximately 284 F. The adsorber discharge fans, one per stage, (centrifugal type induced draft) restore the pressure drop suffered by the flue gas during its passage through the adsorber and associated ductwork. At the Scholz Station, the clean flue gas is directed to a local test stack for emission measurement purposes.

2. Regeneration Section

The purpose of the Regeneration Section is to provide for the continuous on-site regeneration of char which has been loaded with SO_2 in the form of H_2SO_4 .

Regeneration is achieved by contacting the loaded char with hot sand. Sand is utilized as an inert heat transfer media and as such does not take part in the reactions occurring within the regenerator. Its sole function is to supply heat so that the reactions may take place. The mixture (1200 F) of hot sand and char flow slowly downward through the regenerator. Their flow is controlled at the discharge of the regenerator by a char-sand separator-feeder. The char and sand are physically separated by means of a vibrating screen deck (profile wire design). The char is spray cooled to 220 F and returned to the adsorber. The sand is conveyed to a fluidized bed sand heater where heat is added by direct combustion of #2 fuel oil. Both the char and sand streams are closed loop operations.

The flue gas produced by the fluidized bed sand heater is used to preheat the incoming combustion and fluidizing air. After preheating it is returned to the boiler air preheater flue gas inlet for additional heat recovery and to inject the SO_2 produced as the result of combustion into the main flue gas stream entering the adsorber, thereby assuring closed loop operation of this gas stream.

3. RESOX* Section

The purpose of the RESOX Section is to provide for the continuous on-site reduction of sulfur dioxide to elemental sulfur.

The low volume SO_2 rich off-gas, stream is directed from the regenerator to the RESOX reactor which is filled with crushed coal. The SO_2 stream is reduced to gaseous elemental sulfur and the liberated oxygen combines with a portion of the coal carbon to form carbon dioxide. The gases leaving the reactor enter a sulfur condenser where the sulfur is condensed to molten elemental sulfur. The sulfur is collected and stored in an insulated tank which is equipped with steam heating coils to make up for heat losses through the insulation system to maintain the sulfur in a molten form pending shipment via tank truck. The mass-flow coal movement through the reactor is controlled by a discharge feeder. The combination of non-consummed coal and ash is fed into a receiver vessel for ultimate disposal after cooling. The tail gases leaving the sulfur condenser consist of CO_2 , H_2O , N_2 and those remaining "S" values not converted to elemental sulfur. These gases are recycled to the boiler via a centrifugal blower where the sulfur values are oxidized to SO_2 and then re-enter the adsorber allowing complete closed loop operation of the unit. The design of the adsorption section is such as to account for these internal re-cycle loops thereby maintaining a resultant system efficiency consistent with code requirements. In future designs this oxidizing step will probably be done internally with the unit and thus eliminate this connection to the boiler.

III. System Operation

A. General Operating Conditions

During the period from May, 1975 to August, 1975 the system was in a shakedown and/or startup mode of operation. Various pieces of equipment in the Adsorption, Regeneration and RESOX* sections were operated individually and then in combinations to simulate sub-system operation. Finally, the sub-systems were integrated into section operations and the Adsorption and Regeneration sections were operated with passage of flue gas across the Adsorber on August 11, 1975 and continued for a period of 10 days. Table II gives a summary of general operating conditions during the passage of flue gas.

TABLE II
Summary of General Operating Conditions

Boiler Load	15-47 MW
Coal	
Sulfur	1.44% - 3.48%
Heating Value	12,920 BTU/LB. AVG
Flue Gas Entering	
SO ₂ (ppmv)	900-2150
Temperature	235-294 F

RESOX* construction was not complete at this time, thereby requiring that the Regeneration section to run on bypass. The off-gases produced during this period were mixed with the cleaned flue gas from the adsorber and exited the system via the test stack.

The period of operation without flue gas allowed calibration of instrumentation and equipment. It also allowed a period of char dryout which was required due to high moisture content.

B. System Performance

1. Adsorption Section

The operating parameters for the two periods of operation of the Adsorption Section are summarized in Table III.

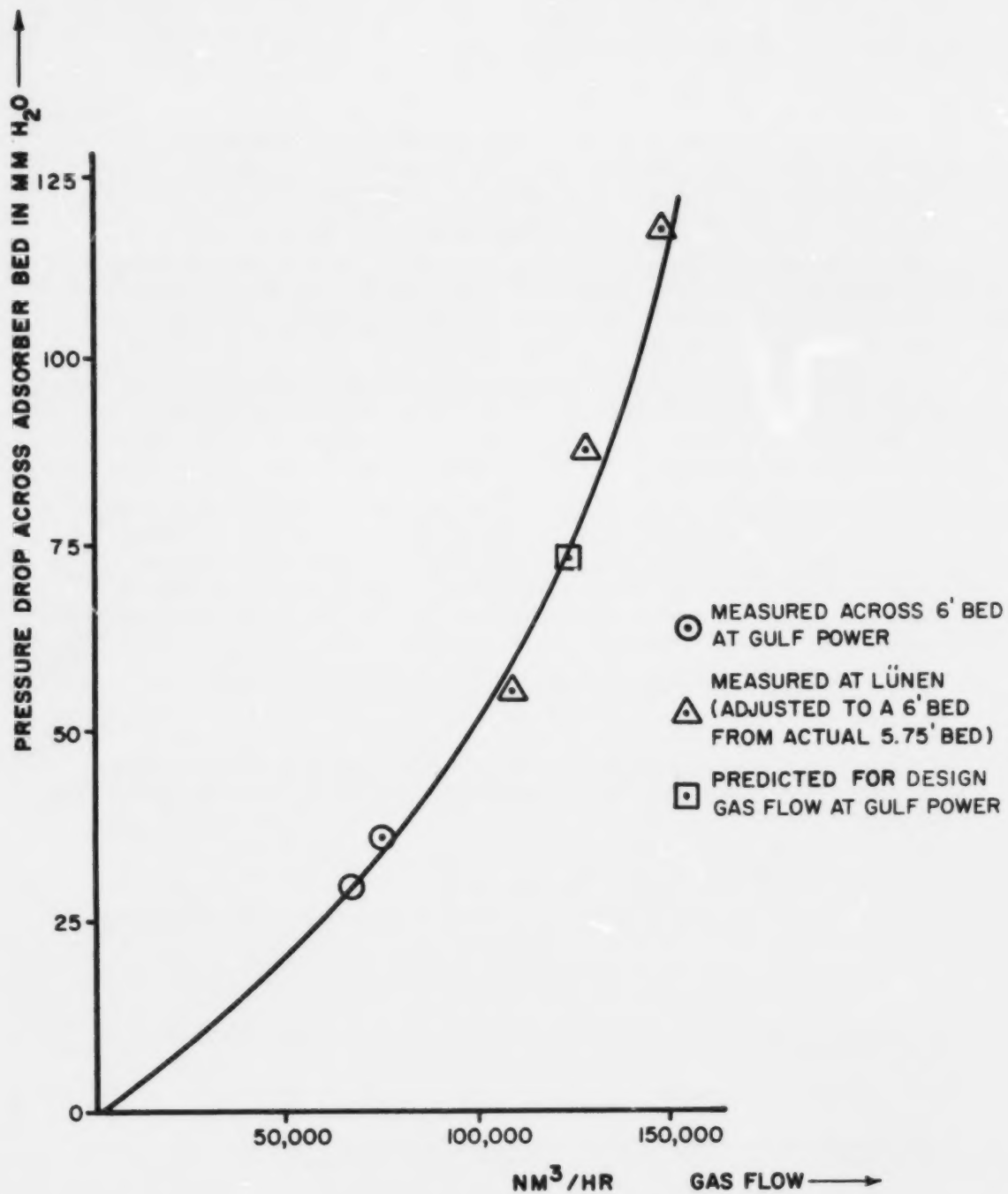
TABLE III
Summary of Adsorption Section Operating Parameters

	<u>w/o Flue Gas</u>	<u>With Flue Gas</u>
Char Flow Rate (LBS/HR)	5000 - 11,850	5300 AVG
Gas Residence Time (Secs)	---	13 AVG
Char Dwell Time (Hrs.)	102 - 43	96 AVG
SO ₂ Removal (%)	---	96 AVG
Gas Flow (LBS/HR)	---	174,000 AVG

Significant and persistent difficulties with char distribution and adsorber char level indication systems made clear that modifications would be required in this area. With the passage of flue gas this was confirmed. Poor distribution causing imbalance in bed levels led ultimately to the shutdown of the system.

The imbalance of char levels throughout the system required portions of the adsorber to be run continuously and others intermittently. This resulted in stagnation of char in certain areas causing local hot spots in several hopper bottom zones. This leads to a reduction in removal efficiency and if not controlled could lead to a dangerous situation. In order to investigate the reasons for this situation the unit was shutdown.

However, despite these difficulties, there were several areas of considerable encouragement. One of these is the fact that actual pressure drops across the adsorber were considerably lower than had been calculated. This confirmed previous measurements on the Lunen unit. Figure 4 shows the relationship between bed pressure drop and flue gas flow. This figure is based on actual measurements taken during the August operational period and subsequent testing conducted in January, 1976. Note that the system pressure drop is quite low. Inasmuch as the adsorber fans represent approximately 80 percent of total system power consumption it may be concluded that our power consumption will be between 0.6 and 1.5 percent of steam generator name plate rating depending on the system design and the mode of operation. This bodes well for future designs which will be able to take advantage of the lower pressure drops in terms of both lower capital and operating costs. Another point of interest is that of SO₂ removal. Removal efficiency is a function of several parameters including SO₂ ppm at inlet, inlet flue gas temperature, char dwell



- Figure 4: Bed Pressure Drop versus Flue Gas Flowrate
Gulf Power Company Demonstration Unit

time and, gas residence time. While the period of operation was too brief to draw final conclusions, certain positive trends can be seen. The averages for flue gas flow and char flow were 57 and 33 percent respectively during the operating period. This gives rise to a gas residence term equal to 217 percent of design. In addition, while char flow rate was only 33 percent of design, it was only flowing 61 percent of the time. Even with these diverse operating conditions, SO₂ removal efficiency was between 96 and 100 percent consistently. The preceding indicates that the char and, therefore, its adsorption capacity, is greater than had previously been anticipated. Of course, additional periods of longer term operation are needed to confirm this point but, if present trends continue an additional reduction in capital and operating costs based on a reduction in size of the Adsorption and Regeneration Sections will be possible.

Finally, there is the matter of flue gas temperature across the adsorber. As previously stated the temperature of flue gas entering the adsorber was in the range of 235-294 F. Other than a brief period, and only for effect purposes, the dilution air fan was not put into service. With an average inlet temperature of 265 F the flue gas outlet temperature ranged from zero to 30 F higher thus providing additional buoyancy at the test stack. This temperature increase in the exit flue gas temperature is a result of the exothermic nature of the adsorption of SO₂.

During the period of operation the Adsorption Section, flue gas treatment, availability was 100 percent and SO₂ removal was well above design values.

2. Regeneration Section

The operating parameters of the Regeneration Section are summarized in Table IV.

TABLE IV
Summary Of Regeneration Section Operating Parameters

Char Flow Rate (LBS/HR)	5300 AVG
Sand Flow Rate (LBS/HR)	180,000 AVG
Sand/Char Ratio (Vol)	13.9:1 AVG
Regeneration Temperature (F)	1200

Here again the period of operation without flue gas permitted calibration of certain instrumentation as well as operational checkout of equipment at varying loads under actual operating conditions of temperature and pressure. There occurred a variety of equipment problems. The most serious result of these was the fact that Regeneration could not be carried out continuously. The specific problems can be divided into four areas: char feed, char/sand separation, hot sand conveying, and char cooling.

Char feeding into the regenerator had been accomplished by means of a rotary airlock (star valve). This proved unsatisfactory for metering purposes and a vibratory feeder was added for flow control. Steam mixing with char fines (plugging the valve) and the jamming of the valve due to the presence of foreign material caused most of the problems in this area.

The design of the char/sand separator was inadequate for the service intended, resulting in frequent outages to repair or replace the screen deck and to reweld various cracks that appeared due to differential thermal expansion between dissimilar metals.

The design of the hot sand bucket elevator called for extremely tight clearances between moving parts at high temperatures. When these clearances could not be maintained it resulted in damage to stationary airlocks and the tripping of the elevator. Once this occurred, regeneration could not proceed until the damage had been repaired.

Difficulty in cooling char resulted from erratic char feed into the regenerator and insensitivity of the control system at low flow rates. These problems resulted in sporadic operation of the cooler at less than optimum efficiency.

As may be seen from the preceding discussion none of the difficulties encountered were related to the process chemistry. To the contrary, the process aspects worked as expected but mechanical problems prevented continuous operation.

As a result the Regeneration Section was only available to the Adsorption Section 56 percent of the time. It should be noted that it is not an absolute requirement that the Regeneration Section be available 100 percent of the time the Adsorption Section is in operation; however, 56 percent availability is unacceptably low.

On the positive side of the ledger, it may be said that when regeneration did occur it was complete. There have been no indications of corrosion due to lingering acid and the majority of the equipment met or exceeded design requirements.

3. RESOX* System

The initial run of Adsorption and Regeneration Sections did not include the RESOX* Section as previously explained. However, two consecutive runs were made in October, 1975. The first without Regenerator off-gas and the second with it. The general operating conditions for both runs are summarized in Table V below:

TABLE V
Summary of RESOX* Section Operating Parameters

	<u>w/o Off-gas</u>	<u>With Off-gas</u>
Coal Flow (LBS/HR)	100-250	100-250
Gas Flow (LBS/HR)	1900	750-2000
Bed Temperature (F)	AMB-1200	1200-1500

The initial run was made to check out gas and coal distribution and temperature controls within the reactor. During this period the previously modified start-up air heater was used to bring the reactor up to reaction temperatures. The function of this start-up heater is to bring the reactor up to the proper temperature range in a scarcity of oxygen so as to obtain proper temperature control in the reactor. Therefore, the heater, which burns number 2 oil with air, does not use secondary air for a diluent, but rather steam. Thus the heated flue gas produced is essentially inert and very low in oxygen content (0.5-1.5%).

Once the reactor was brought up to temperature and all control functions were tested, the Regeneration Section, operating in a hot idle mode, was brought on line by the introduction of saturated char into the regenerator. Due to the limited amount of saturated char (approximately 13 hours worth at a 33% char flow rate), the RESOX* run with off-gas was necessarily brief. All of the char previously saturated had already been regenerated. Only the amounts left in the various surge tanks was still saturated. In order to compensate for the low flow of off-gas, the start-up heater was left in service.

This resulted in a diluted off-gas stream entering the RESOX* reactor. However, the test showed that the RESOX* reaction is controllable and responded very nicely to the controls system. The control system monitors temperature profile in the reactor and then uses control air to increase temperature or steam to dampen the temperature. By this method a reaction zone can be maintained at the proper level in the reactor.

Even with the start-up heater in service the flow of gas through the sulfur condenser was too low for proper operation of the condenser. The sulfur produced would not condense as a liquid, but rather was subject to shock cooling resulting in the production of a sulfur mist which passes through the condenser without being collected.

After the heater modifications the RESOX* Section was operated with few problems and these were all of a minor nature. Because the difficulties in the Regeneration Section, discussed above, had not yet been resolved totally, we encountered a repeat of some of those problem areas during the RESOX* runs.

IV. Modifications Program

The preceding section presented the major difficulties encountered in each part of the system. In this section we will examine the solutions to these various problems. As pointed out previously, no major process problems were encountered during the initial runs and it is not anticipated that any will present themselves during the testing program.

1. Adsorption System

The major problem areas in the Adsorption Section were related to char distribution and level control. To overcome these difficulties the char distributing conveyors on top of the adsorber were replaced with a "spider leg" system. This system accepts char from the regeneration section via a bucket elevator and oscillating conveyor and deposits it in a right regular cylindrical tank atop the adsorber. From there it is fed by gravity through a series of ten 8 inch pipes into the eight first stage beds and the four second stage beds (one pipe per two second stage beds). Each pipe or "spider leg" is provided with a sight glass to observe flow in that leg. These legs enter the top of the adsorber so as to be positioned above the geometric center of each bed. This arrangement obviates the necessity for individual level controls on each bed and transfers total control over char level to the adsorber bottom extraction feeders. Running these feeders at the same feed rate ensures that all portions of the beds move down at an equal and continuous rate. Overall level observation is then made via a single nuclear level detector in the new surge tank. The level detector has a single source with two pick-ups, one for high level and the other for low level. This new system has been tested and functions as predicted.

In addition, numerous new thermocouples have been added at various locations in and around the adsorber to allow better monitoring of temperature distribution within the adsorber and, in effect to act as a check on char and gas distribution. These thermocouples have now provided confirmation that both gas and char are being distributed evenly assuring maximum removal efficiency.

2. Regeneration Section

The four areas of equipment malfunction in the Regeneration Section and the corrective action taken are as follows:

a. Char feeding

(1) A vibratory feeder and sight glass were added upstream of the star valve. This provides for a continuous smooth feed rate to the star valve obviating the requirement for the valve to act as a feeder. It now only acts to seal or lock. In addition a TV camera was installed at the sight glass so that changes in the vibratory feeder feed rate can be monitored in the control room.

(2) To avoid foreign material from jamming the feeder a removable scalping screen has been added at the inlet of the star valve.

(3) To prevent steam from plugging the star valve the regenerator operating pressure has been modified to slightly negative pressure as opposed to slightly positive pressure. In addition a new flyash removal system was installed. This system was added to the scope of supply too late to be installed for the earlier shadesown runs. It's inclusion prevents the carryover of fines to the regenerator. This eliminates the problem of plugging in the star valve when steam is present.

b. Char/Sand Separation

The modifications made to the char/sand separator include the following:

(1) A profile wire screen replaced the existing woven cloth screen. This eliminates screen failure from relative motion between the pan and the screen caused by the inability to maintain proper screen tensioning at operating temperatures. The profile wire screen is rigid and does not require tensioning.

(2) The channels that connect the hot stainless steel pan section and the relatively colder carbon steel support frame and drive assembly have been replaced. New connection clips allow structural integrity to be maintained while allowing for thermal expansion when joining stainless steel to carbon steel.

(3) A revised insulation system to minimize thermal gradients in the pans and its cover has been applied. The previous insulation system was adequate for the temperatures involved but, could not withstand the constant vibration. The new system consists of two inches of insulating blanket compressed on studs to 50 percent of its original thickness. This in turn is covered with expanded metal mesh and aluminum lagging. The compression is made possible by large washers and nuts placed outside of the lagging. The result is a rigid insulation system that moves with the vibrating part without motion relative to it. To date, the insulation system has performed satisfactorily.

c. Sand Conveying

The original design of the hot sand bucket elevator called for a system of intricate airlocks that separated the 1200 F sand being conveyed in the buckets from the chain which was to operate at a maximum temperature of 800 F. This was accomplished by the separation of chain and bucket with a labyrinthine passageway and the injection of cooling air in the area of the chain. Actual operation proved that the clearances involved in the airlocks were unacceptably close causing interferences between the moving chain and buckets and the stationary airlocks and resulting in damage to the buckets and the airlock. It was further observed that no cooling air was required to maintain the chain temperature below 800 F. It was therefore decided to eliminate a portion of the airlock labyrinth thus eliminating the source of interference. Operation after this modification has been perfect and no cooling air has been used.

d. Char Cooling

The insensitivity of the control system has been alleviated by the changout of the water control valve with one of greater linearity making the valve response more even over the control range i.e., finer, more even transition in valve opening versus signal input. In addition, the use of steam temperature as an inferential measurement of exit char temperature as opposed to direct char temperature measurement has been installed. These two improvements coupled with a more even char flow have resulted in adequate and controllable char cooling.

3. RESOX* Section

The only modifications made in the RESOX* Section in the period following initial operation were the installation of added alarm points, and the wring-out of existing control loops in the boiler feed water and steam circuits.

Due to certain wiring errors two circuits could not be placed in the automatic mode and required manual operation. This caused wide variations in both condenser water level and condenser steam pressure. These deficiencies have been corrected and the system now operates on automatic controls with good stability.

V. Calendar of Operations

The modifications program outlined in the preceding section commenced in late August 1975 and continued through January 1976 with the exception of the five day RESOX* operation in October 1975. January and part of February were devoted to a systematic testing of the modifications. This testing program is outlined in Table VI.

With the completion of the pre-startup testing program the unit was declared ready for the introduction of flue gas and all materials handling loops as well as the RESOX* loops were put into continuous operation at operating temperatures and pressures for a three-day period prior to the introduction of flue gas to ensure stability and continuity of operation.

With the re-introduction of flue gas the operations at Scholz Steam Plant entered a new phase, system testing.

Because of the long delay in obtaining successful operation, the Scholz program is nearing the end of the timetable and budget provided by the Southern Company. Consequently a test program has been organized to work within these constraints. Any future operation of the system will depend heavily on the success of this program. The schedule is outlined in Table VII.

TABLE VI
Modifications Testing Program - January 1976

<u>Test #</u>	<u>Name</u>	<u>Test Objectives</u>	<u>Results</u>
1	Air Test	To calibrate all gas side flow measuring devices, establish pressure drop vs. gas flow characteristics, establish gas distribution	All test objectives were met.
2	Hot Sand Circulation	To test modifications to components in the hot sand loop, and to provide data for component calibration	All test objectives were met.

TABLE VI (Continued)

<u>Test #</u>	<u>Name</u>	<u>Test Objectives</u>	<u>Results</u>
3	Hot Sand/ Char Circulation	To test the revisions made to the char cooler and provide data for future control loop modifications. Test was to use "old" char/sand separator.	Test was cancelled due to late start and interference with other operating/modification schedules test re-scheduled.
4	Char Circulation	To test spider legs distribution system and calibrate various pieces of char handling equipment. Also, to provide testing of newly installed fines removal system.	All test objectives were met.
5	Hot Sand/ Char Circulation	To test new char/sand separator. Added Requirements of test #3 previously	All test objectives were met.
6	RESOX Steam BFW Circuit Test	To test the ability of these circuits in the automatic mode.	All test objectives were met.

TABLE VIILong Term Testing Program

Flue Gas Condition

<u>Test #</u>	<u>Name</u>	<u>Fuel Sulfur (%)</u>	<u>Load</u>	<u>Ash</u>	<u>Duration</u>
1	Startup	3-4	Constant	No	4 wks
2	Var I	3-4	Constant	No	4 wks
3	Var II	3-4	Fluc.	No	4 wks
4	Var III	3-4	Constant	Yes	4 wks

The objectives of the above testing program are to determine:

- a. SO₂ removal performance
- b. NO_x removal performance
- c. Flyash removal performance
- d. Operating and Maintenance costs
- e. System reliability

Inasmuch as this paper is being written in advance of the formal testing program, due to Symposium deadlines, the outcome of the tests will be the subject of future reports. At the Symposium we hope to be able to share with you some of the early data taken in February.

VI. Conclusions

Based on the foregoing it is fair to conclude the following points:

- A. Early start-up operations were slower and less successful than desired.
- B. Brief operations in August and October of 1975 did not show any process deficiencies. To the contrary they showed the process to be viable. However, longer term observations of process variables must be conducted to verify the early results.
- C. All of the difficulties encountered to date have been mechanical and initial testing indicates that these have been corrected.
- D. Early test results have indicated the capability for reduction in both capital and operating cost factors due to lower than predicted pressure drop and higher than expected char loading performance.
- E. System reliability has not been demonstrated as yet but, with the modifications testing successfully completed the unit will be run integrated for an extended period to demonstrate this point.

PART II

BF-STEAG DEMONSTRATION UNIT

OPERATIONAL EXPERIENCE AND PERFORMANCE

I. Introduction

With the financial support of the Federal Ministry of the Interior, Bergbau-Forschung is presently operating a demonstration plant for the desulfurization of flue gases. The plant accepts 150,000 M³n/hr. (88,275 CFM) of flue gas in the form of a slipstream from a 350 MW coal fired boiler owned and operated by STEAG at Kellermann Power Station in Lunen, Federal Republic of Germany.

The flue gas is desulfurized, without cooling, in a temperature range of 110 to 160 C (230-320 F). The captured SO₂ is converted to elemental sulfur.

This prototype demonstration unit is the largest dry desulfurization plant operating thus far in the Federal Republic of Germany.

The only effluents emanating from the unit are utilizable and/or disposable sulfur, cooling water, dry flyash and, small quantities of char fines. The flyash is that which is captured in the adsorber, which is located downstream of a high efficiency electrostatic precipitator.

II. Development of the Process

The long known principle of the process is the adsorption of SO₂ on carbonaceous adsorbents and its conversion to sulfuric acid by means of combining with oxygen and water vapor also present in the flue gas. The sulfuric acid is enriched adsorptively in the pore system of the carbonaceous adsorbent. This adsorbent material, called char, loaded with sulfuric acid is thermally regenerated. In this portion of the process the acid is decomposed to SO₂, CO₂, and H₂O with the consumption of carbon. The SO₂ rich gas thus produced is then further processed as desired.

When Bergbau-Forschung started their work in 1965 for the development of a process for the adsorptive desulfurization of flue gas, the first problem was to develop a suitable carbonaceous adsorbent. The activated char which was developed is characterized by a high abrasion resistance, a particle size that guarantees low pressure drop in the adsorber (9 mm ϕ), a very low reactivity with oxygen, and a high SO₂ adsorptive capacity.

During the development of the process, the thermal regeneration concept was studied in particular to obtain conditions that would not result in a loss of activity of the activated char but, would result in an increase in the level of activity up to some higher equilibrium value. Regeneration is accomplished in the temperature range of 500 to 650 C (932-1202 F). The heat is supplied by sand which acts as an inert heat transfer media. Thus a regeneration temperature with a high heating-up velocity can be achieved. This results in a regeneration reactor which is small in volume and has short char residence times. In addition side reactions, e.g., with oxygen, which would consume additional char, can be eliminated. It is a special and important advantage that the regenerator off-gas is obtained in an undiluted condition and has, thus, the highest possible concentration. Therefore, the SO₂ in the flue gas low concentrations (0.1 to 0.2% by volume), can be concentrated up to more than 30 percent by volume. This SO₂ rich gas can then be further processed to liquified SO₂, sulfuric acid, or elemental sulfur.

III. Technical Description of the Demonstration Plant

The demonstration plant in Lünen is comprised of three main components, viz., the desulfurization reactor, the regeneration plant, and a modified Claus plant for the processing of SO₂ rich gas to elemental sulfur. Figure 5 shows the desulfurization reactor (adsorber) designed in the form of a travelling bed reactor with traverse gas flow. The beds of activated char are placed in a circular silo. The flue gas from the boiler flow into the center of the reactor and then radially outward through the beds of activated char. The beds are each 1.75 m (5.74 feet) thick and the motive force for gas flow is provided by an induced draft fan on the flue gas outlet of the reactor. The char moves slowly from top to bottom between sets of fixed louvers. Freshly regenerated char is continuously added to the top of the reactor and loaded char is continuously drawn off at the bottom of the reactor and conveyed to the regeneration plant.

The degree of desulfurization can be varied by means of the residence time of the char in the adsorber thereby allowing the desulfurization plant to follow boiler load.

The flyash collected in the adsorber along with char fines are separated by screening prior to regeneration. Loaded char is conveyed to the regeneration plant via bucket elevators.

The regeneration plant is shown in Figure 6 and is also designed as a travelling bed reactor. The loaded char is directly mixed with hot sand at a temperature of between 650 and 720 C (1202-1328 F) which results in a mix temperature of 500 to 650 C (932-1202 F) depending on the temperature of the incoming sand. This mixture moves through the reactor in 10 to 20 minutes and is then discharged onto a vibrating screen deck to separate the two solid components. The char is then cooled and returned to the adsorber for another cycle of adsorption. The heat required to restore the sand to its proper temperature is provided by means of combustion gases which also act to pneumatically convey the sand to the top of the regenerator.

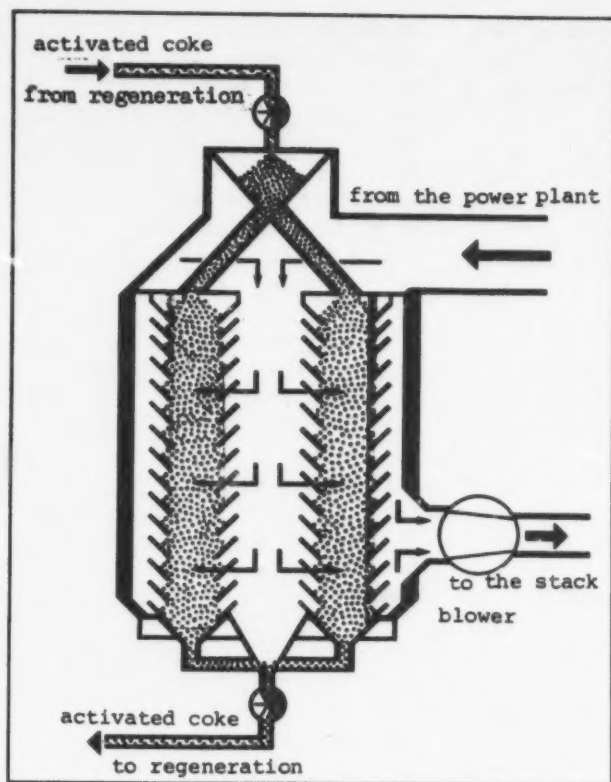
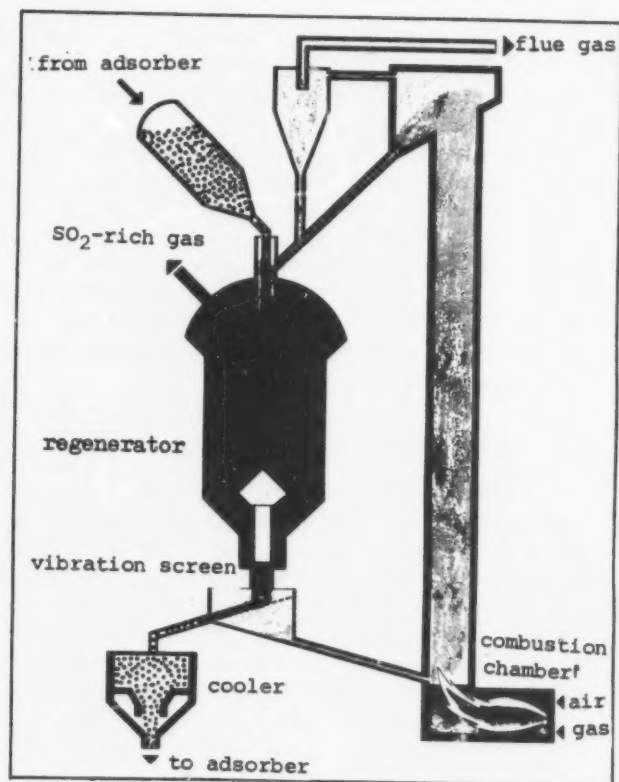


Figure 5: Adsorption Section - Lünen

Figure 6: Regeneration Section
Lünen



The SO₂ rich gas emits from the upper part of the regenerator reactor and is drawn off to the Claus unit. In this plant, shown schematically in Figure 7, a certain percentage of the SO₂ rich gas is reduced to H₂S with town gas in a special reduction chamber. This H₂S is then combined with the remainder of the SO₂ in a three stage contact plant with the resultant production of elemental sulfur. The sulfur is collected as a liquid after condensation and is stored in a heated tank. The Claus unit is operated at an efficiency of between 90 and 94 percent. The remaining unconverted "S" values are incinerated back to SO₂ and returned to the inlet of the adsorber.

In order to get a better concept of the entire unit Figure 8 shows the integration of the three plant sections with respect to the power plant. As can be seen from the left side of the figure, flue gas is withdrawn downstream of the electrostatic precipitator (1), flows through the adsorber (2), and is returned to the main flue gas duct prior to entry into the power plant stack. It is also possible to take flue gas upstream of the electrostatic precipitator through a duct not shown in the figure. This allows for the study of the simultaneous removal of flyash and SO₂. The concentration of inlet flyash can be as much as 5 g/m³. In the center of Figure 8, the regeneration plant is shown. Of interest to the energy balance of the unit are a heat exchanger (18) for the utilization of waste heat from the sand heating and conveying loop and a second heat exchanger (14) for the partial recovery of waste heat liberated during the cooling of the char. The Claus plant is shown on the right side of the figure where SO₂ rich gas is drawn off from the regenerator (11) to the reduction burner (20). The waste gases from the tail gas incinerator (28) are taken back to the adsorber (2).

An aerial view of the unit is shown in Figure 9. It shows a portion of the 350 MW Kellermann Power Station of STEAG, as well as the entire desulfurization unit. The flue gas enters the circular adsorber at the top and leave near the bottom via an induced draft fan and from there to the power plant stack. The regeneration plant is contained in the rectangular tower. The SO₂ rich gas leaves the regeneration plant via the vertical pipe seen on the side of that structure. The Claus plant (partially hidden by coal conveyor) is in front of the adsorption and regeneration section. Figure 10 shows a general view of the unit. The entire unit is centrally controlled and monitored from the control room shown in Figure 11. Inasmuch as this is a demonstration unit, a multitude of data is recorded and/or monitored which will not be required in a commercial unit.

IV. Commissioning and Initial Results

The adsorption and regeneration sections of the unit were designed and constructed by Deutsche Babcock and Wilcox AG of Oberhausen in accordance with the basic engineering provided by Bergbau-Forschung. The modified Claus plant was designed and constructed by Davy Powergas. The order for incorporation of the entire plant into the power station was placed with STEAG. After completion of the entire plant, commissioning of individual loops was started early in the summer of 1974. Difficulties were experienced with vendor supplied equipment such as bucket elevators

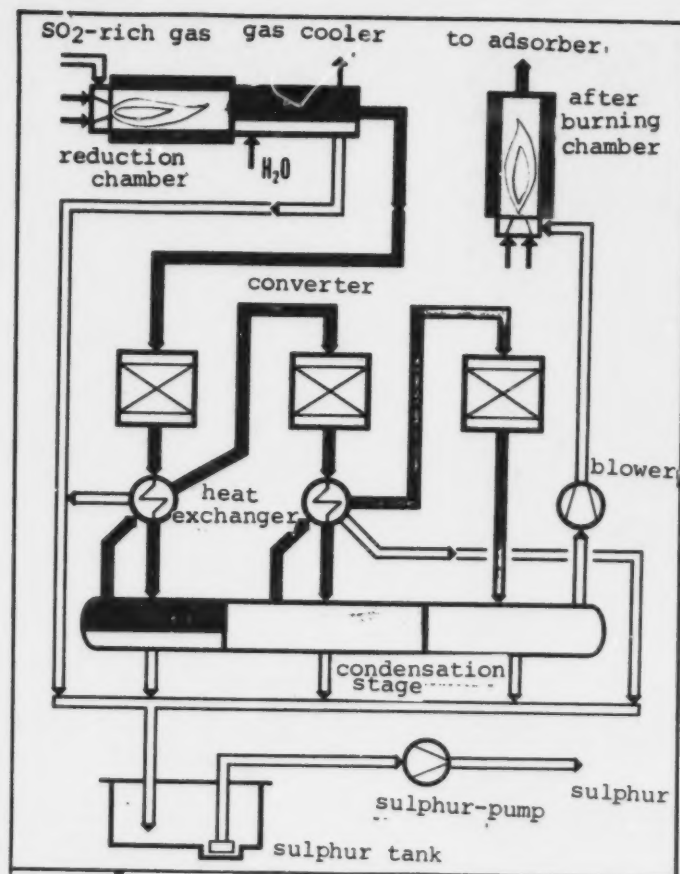


Figure 7: Modified Claus Unit
Lünen

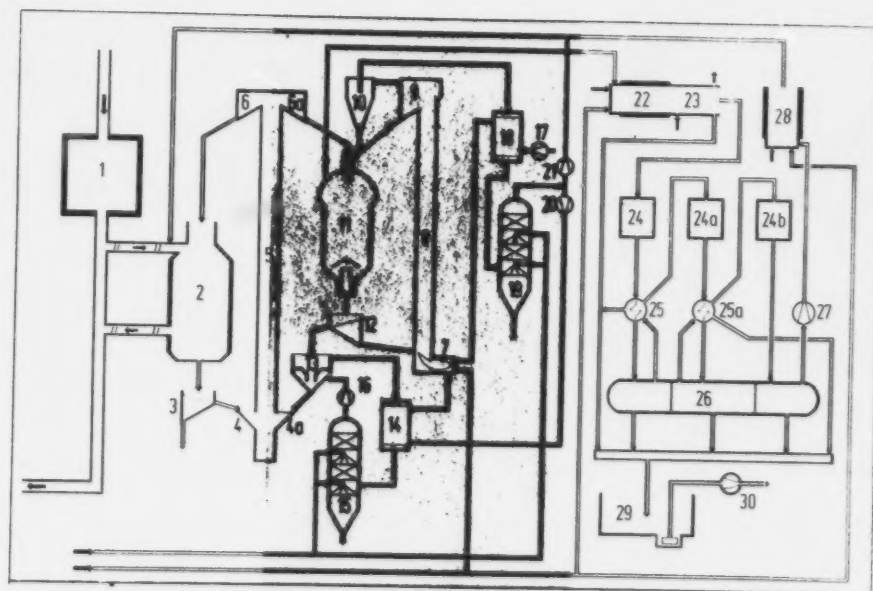


Figure 8: Flowsheet of prototype plant in Lünen

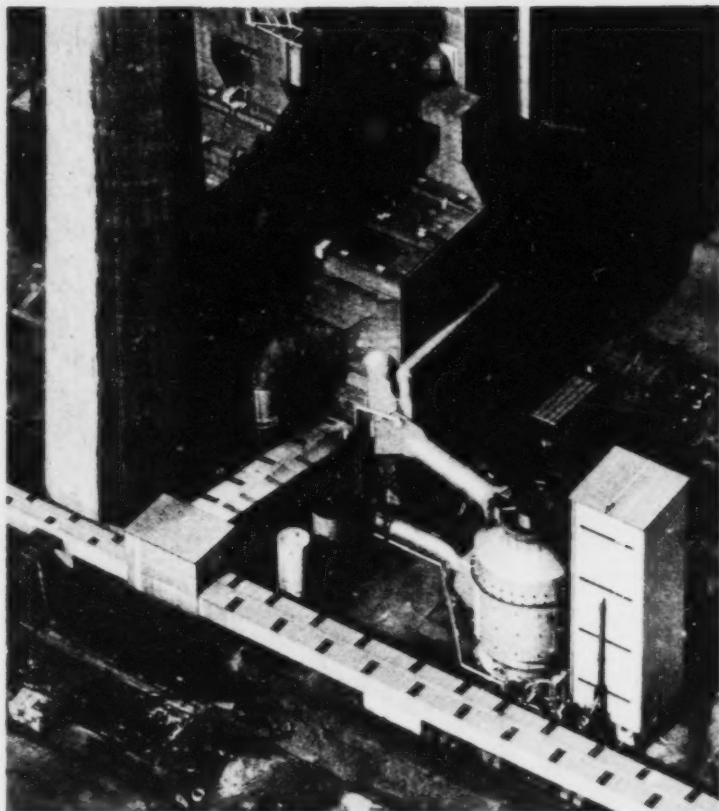


Figure 9: Aerial view of
Kellermann Power Station
Lünen with desulfurization
unit in foreground

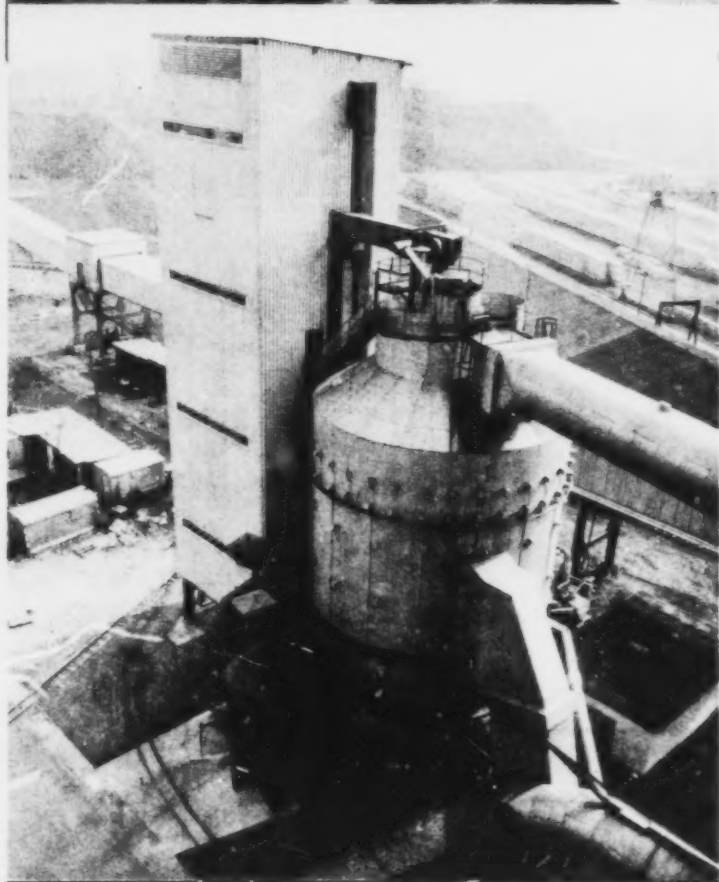


Figure 10: View of BF unit
at Lünen

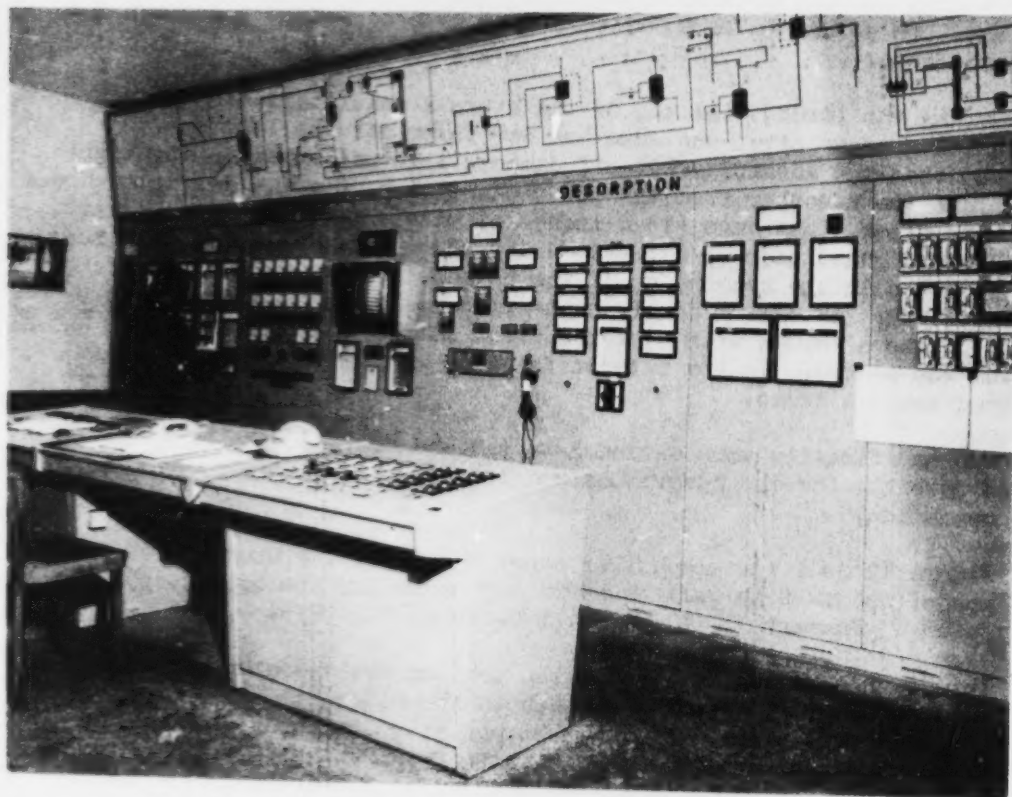


Figure 11: Desulfurization Plant Control Room - Lünen

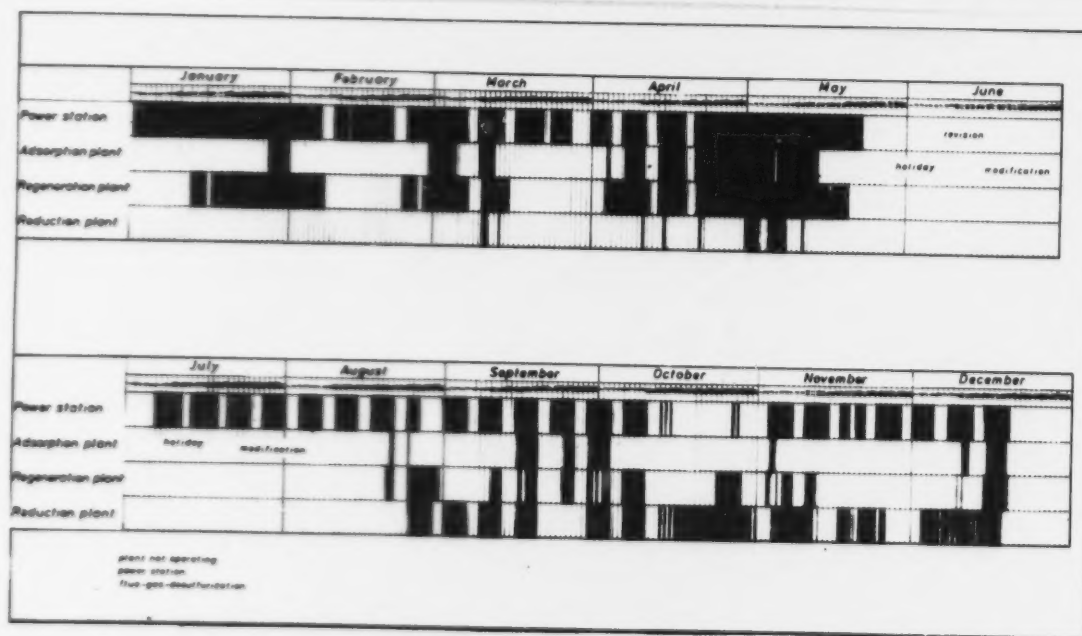


Figure 12: BF unit - Lünen - Operating Hours

and fans. These had to be modified and/or changed before the operation was satisfactory.

During the first trial run of the overall desulfurization plant, difficulties arose after the adsorber was taken off the line due to the fact that the adsorber shut-off dampers were not sufficiently tight to isolate the adsorber from the power plant stack draft. Due to a vacuum of 350 mm water glass gage (13.8 inches of water) caused by stack draft, uncontrolled quantities of air were drawn through the adsorber char beds. This resulted in the heating up of the char beds due to the adsorption of oxygen. By installing double shut-off dampers at the inlet and the outlet of the adsorber with a vacuum break between the dampers the problem was solved. In the interim the safe operation of the plant was achieved several times.

The modification work extended to the end of 1974. By early 1975 it was possible for the adsorption and regeneration plants to be put into operation.

Figure 12 is a bar graph that shows the operating hours of various sections of the unit as well as operating hours for the boiler, for the period of January 1, 1975 through December 31, 1975.

During this period the adsorption section was operated with flue gas for 1,450 hours while coupled to both the regeneration section and the power plant. Further the adsorber was started up and shutdown 15 times in connection with the power plant. This cycling operating is due to the fact that the power plant is operated as a peaking unit. The regeneration plant was run for a longer period of 2,850 hours. The reason for this was optimization work required before integrating all three sections of the plant. The modified Claus unit (reduction plant) was operated for 480 hours including 320 hours on model gas.

Figure 13, shows some results for the period from February 28, 1975 to May 15, 1975, during which period flue gas was taken from the power plant to the desulfurization plant for a total of 1,000 hours. In the upper portion of the figure the inlet and outlet SO_2 concentrations are given. In the central portion desulfurization efficiency is plotted along with the char flowrate. The through-put of flue gas is shown at the bottom. During this 1,000 hour period of trouble free operation the through-put of flue gas varied between 100,000 $\text{M}^3/\text{hr.}$ and 170,000 $\text{M}^3/\text{hr.}$ (58,850 CFM and 100,045 CFM) and the char flowrate varied from 3.5 to 7.5 M^3/hr (124 to 265 ft^3/hr). This corresponds to a char dwell time in the adsorber of from 40 to 90 hours. As a result of these operating parameters the degree of desulfurization varied between 65 and 99 percent. The measured values in this chart were plotted as daily mean values.

Figure 14, on the other hand shows the effect of short term variations of SO_2 inlet concentrations on the degree of desulfurization and adsorber outlet flue gas temperature. These results were obtained while holding flue gas flow constant at 150,000 $\text{M}^3/\text{hr.}$ (88,275 CFM) and char dwell time constant at 50 hours. During this period inlet SO_2

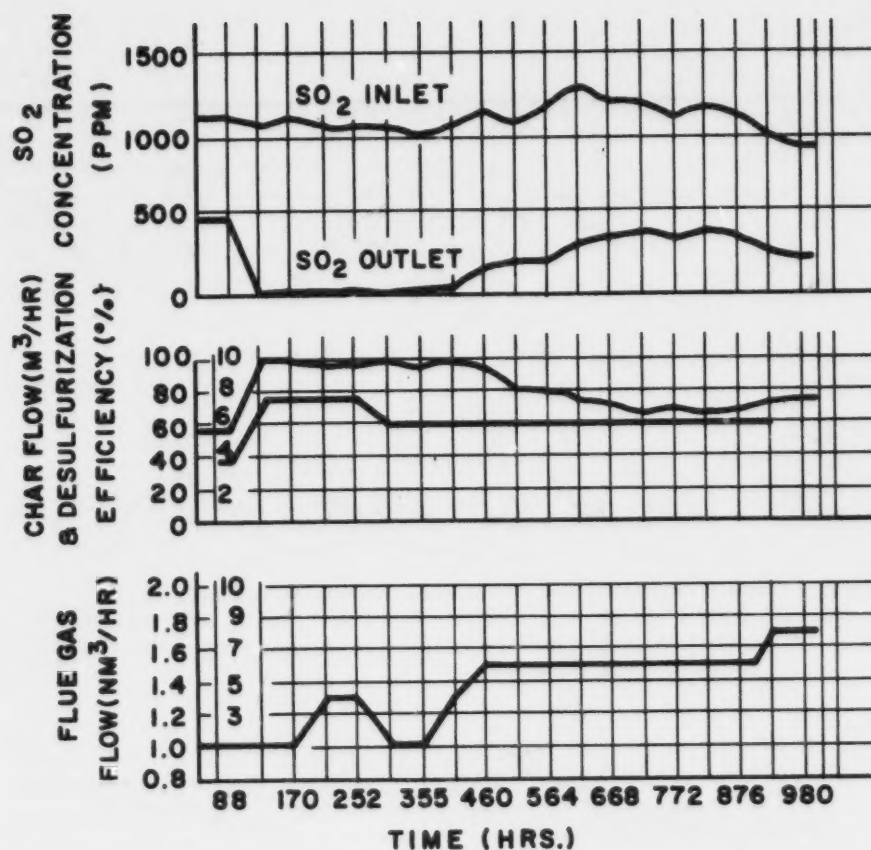


Figure 13: Various operating parameters vs. time for a 1000 hour test run at Lünen

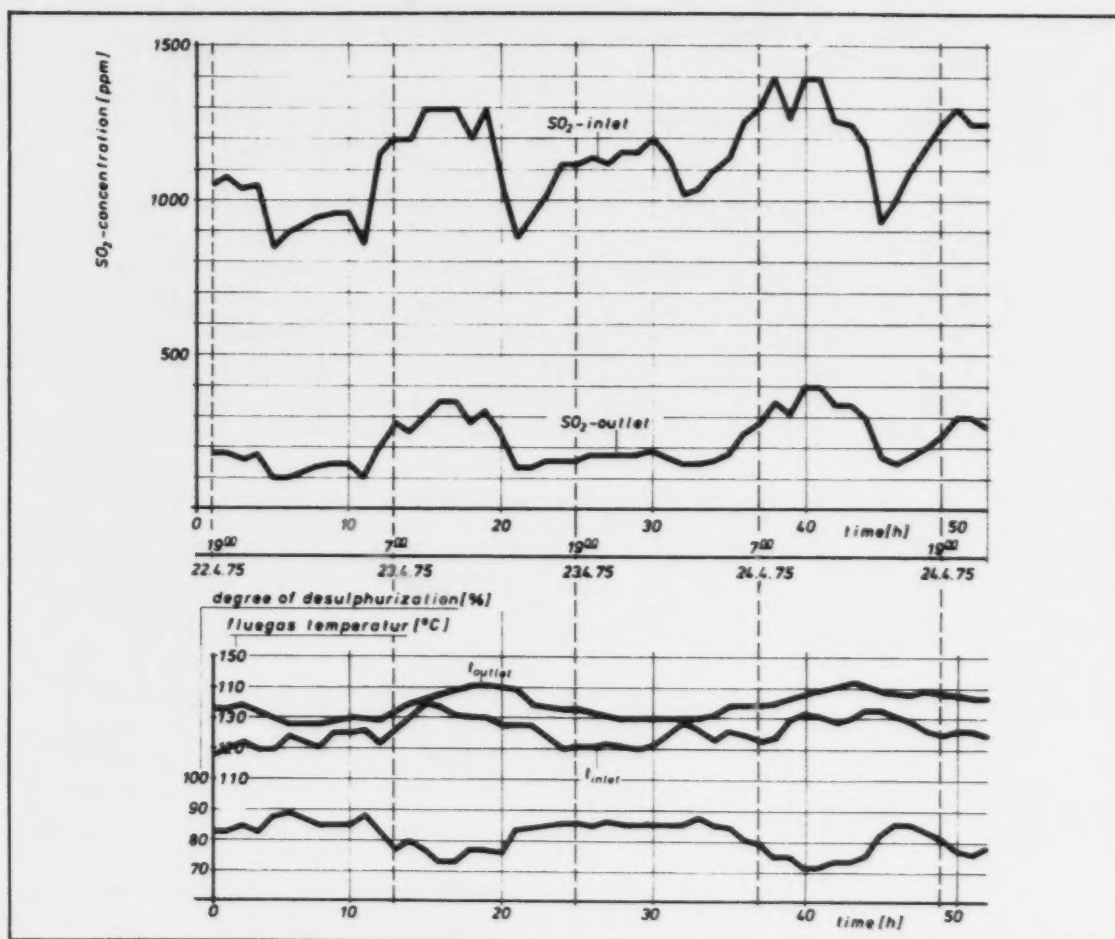


Figure 14: Effect of short term variations of inlet SO_2 concentration on the degree of desulfurization and outlet gas temperature

concentrations varied between 850 and 1300 ppm with outlet concentration of 100 and 400 ppm respectively. Hence a degree of desulfurization varied between 77 and 99 percent. The inlet flue gas temperatures were between 118 C and 135 C (244 F and 275 F) depending on the load on the power plant. Due to the reaction heat, the outlet flue gas temperature varied between 128 C and 142 C (262 F and 288 F). In this case the char dwell time was kept constant. Without stating the dwell time the degree of desulfurization can be improved and adapted to any desired value independent of the load fluctuations in the power plant.

Figure 15, shows the relationship between pressure drop across the entire adsorber and flue gas flow rate. With a flue gas flowrate of 110,000 M³n/hr. (64,735 CFM) the pressure drop is 85 mmWG (3.3 inches of water) and with a flowrate of 170,000 M³n/hr. (100,045 CFM) the pressure drop is 160 mmWG (6.29 inches of water).

As the coal fired power plants of the Federal Republic of Germany cover only peak loads, they must change their loading frequently in the course of the day and, as a rule, shutdown entirely during the weekends. Therefore, high demands are placed on the flue gas desulfurization plant with regard to flexibility. The test results obtained thus far with the Bergbau-Forschung process show that the process can be adapted to variations of loading without difficulty and that it can be started up and shutdown simultaneously with the power plant.

In the event the desulfurization process must be interrupted for a longer period, the activated char can be regenerated and cooled down to 50 C to 60 C (122 F to 140 F). In the case of short term interruptions in the supply of flue gas, e.g. during weekends, it has shown to be advantageous not to cool down but, rather to add only inert gas to the adsorber. The frequent starting up and shutting down to the demonstration plant in Lünen proved that only small quantities of nitrogen are necessary for this. This type of operation has the advantage that the downstream reduction plant need not be shutdown, but can be continued in operation at reduced capacity. To operate in this mode the activated char loop has to be circulated at a reduced rate via the regeneration plant. When flue gas flow is restored, the circulating activated char can be kept at reduced flow rate for several days with the same degree of desulfurization as that prior to the interruption in the supply of flue gas.

V. Conclusion

As can be seen from the preceding, the results of this demonstration plant clearly establish not only the viability of the process, but also the high degree of desulfurization and low pressure drop capabilities. They further show the flexibility of the unit in a difficult power plant application. During operation of the demonstration plant at Lünen in 1976 we will continue to demonstrate this dry adsorption system and hope to be able to share the results of new testing programs with you at a future meeting.

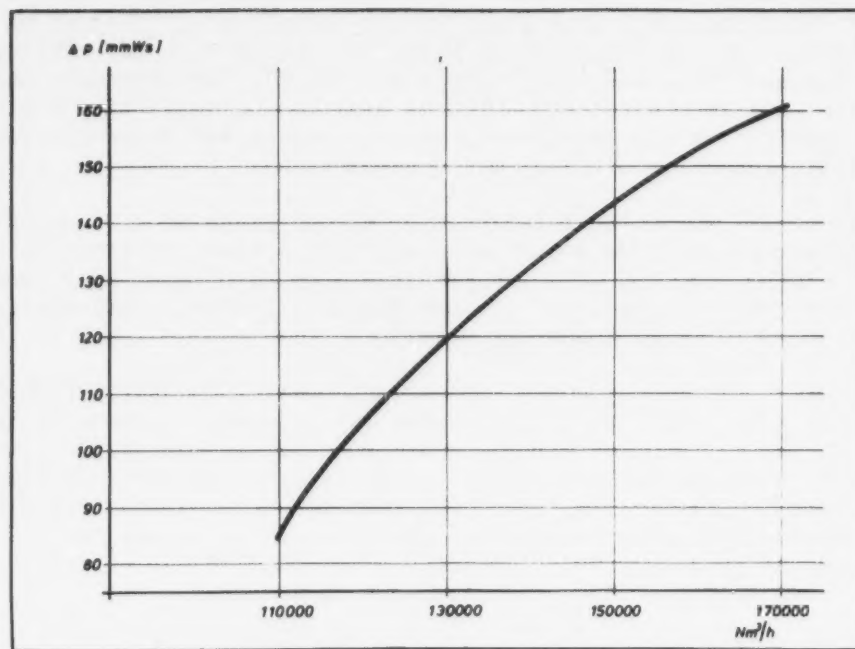


Figure 15: System pressure drop vs. flue gas flow rate

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the United States Environmental Protection Agency for their invitation to present these results to the Symposium. Further, we wish to note the spirit of mutual cooperation between Gulf Power Company, Southern Services, Incorporated, Bergbau-Forschung, GmbH and Foster Wheeler Energy Corporation. Without this cooperation this report would not have been possible.

THE CONSOL FGD PROCESS

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ABSTRACT

This paper describes a new regenerative process for the removal of 95% or more of sulfur dioxide from power plant stack gases. Scrubbing is conducted by circulation of a concentrated aqueous solution of potassium thiosulfate through a pump-around loop containing a packed bed scrubber for SO_2 removal and an external reaction drum.

A solution containing a mixture of hydrosulfides, polysulfides, carbonates and bicarbonates is injected into the circulating salt solution just ahead of the reaction drum. The hydrosulfides and polysulfides are quantitatively removed from the circulating salt solution before entering the scrubber by reaction with sulfites formed in the scrubber to produce thiosulfate.

The carbonates in the feed solution pass through the reaction drum unconverted, but react in the scrubber with SO_2 to produce the aforementioned sulfites. The net product from the scrubbing process is thus potassium thiosulfate.

The scrubber feed solution is produced by noncatalytic reduction of the thiosulfate with a CO-rich gas. H_2S is simultaneously produced which is converted to elemental sulfur in a Claus plant.

A very low by-product sulfate yield of about 1% of the SO_2 absorbed and very high SO_2 removal efficiency as high as 99% in a simple single-stage scrubber were achieved. The scrubbing solution is a clear salt solution which provides for excellent operability in the scrubber which is free of problems due to scaling and deposition of solids.

The scrubbing process was demonstrated on both a 1000 ACFM and a 30,000 ACFM pilot plant. The latter plant operated with flue gas drawn from a coal-fired power plant of Philadelphia Electric Company. Regeneration of the spent reagent was demonstrated in a separate pilot operation. Finally, closed-loop operation was demonstrated with continuous circulation of reagent between the regeneration and the 1000 ACFM scrubbing pilot plants.

An economic analysis showed the process to be competitive with other regenerable processes.

THE CONSOL FGD PROCESS

INTRODUCTION

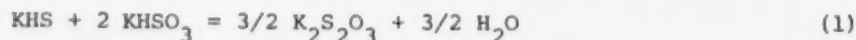
The original aim of this project was further development of the aqueous potassium formate process reported by Yavorsky, et al in 1970⁽¹⁾. The process chemistry, as a result of concurrent laboratory research, was modified and simplified early in the course of the study. The new scrubbing process was demonstrated both in a 1000 ACFM pilot plant at the Research Division of Consolidation Coal Company in Library, Pennsylvania, and in a 30,000 ACFM pilot plant located at the Cromby Power Plant of Philadelphia Electric Company. A regeneration pilot plant was also built and operated at Library. The two units at Library were operated together in closed-loop, integrated fashion in the final phase of the program.

PROCESS DESCRIPTION AND DEVELOPMENT HISTORY

Figure 1 is a schematic flow sheet of the scrubbing system and corresponds to both the Library and the Cromby pilot plants. A venturi scrubber was used in each unit to quench and humidify the hot flue gas. It served also to remove the SO_3 , HCl and any residual particulate matter from the flue gas.

The scrubber itself is a packed tower with a pump-around circuit through a reaction drum. Fresh feed, spent scrubber product and make-up potash are fed and withdrawn from the scrubber system as shown. The solid lines indicate the feed and withdrawal points as practiced in the pilot plant operations, the dotted lines indicate the preferred points for a commercial system.

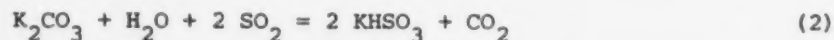
The key reaction in the Consol process is the one that takes place in the reaction drum. Experiments confirmed previous literature data by Hansen and Werres in 1933⁽²⁾ that sulfite reduction to thiosulfate may be effected by use of KHS as a reducing agent, i.e., by the reaction:



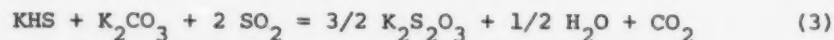
Similar reactions occur with polysulfides and sulfite.

The feed to the scrubber system is an aqueous solution containing KHS, K_2S_x , KHCO_3 , K_2CO_3 and KOOCH produced in the regenerator by reduction of the thiosulfate scrub product with CO . The polysulfides and KOOCH are relatively minor components. The polysulfides are consumed in the reaction drum while the KOOCH is substantially inert under the conditions of the process. The feed enters the reaction drum where it is mixed and reacts with the circulating scrub solution. Conditions are imposed such that the KHS and K_2S_x are completely consumed in the reaction drum via reaction (1) and the corresponding reaction for K_2S_x . A residence time of less than 1.5 min is sufficient at a pH of 7. Complete consumption of KHS is desirable since, if it is allowed to enter the scrubber, some evolution of H_2S into the stack gas occurs.

The actual removal of SO_2 in the scrubber occurs by virtue of reactions with carbonates in the feed solution as, for example,



The overall reaction in the scrubbing system is now the sum of reactions (1) and (2), and may be written as reaction (3) for the KHS and K_2CO_3 .



Similar equations apply for polysulfides and bicarbonate.

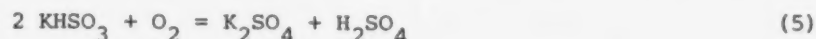
Control of the scrubbing process is effected in two ways. The first is by controlling the rate of the fresh scrubber feed to maintain the pH in the scrubber effluent at about 7. This insures nearly complete SO_2 removal as well as quantitative removal of the KHS and K_2S_x from the feed reaction drum via reaction (1). The second is to control^x the composition of the scrubber feed to maintain the proper proportions of KHS and K_2S_x with reference to the content of K_2CO_3 and KHCO_3 . The stoichiometric relationships may be expressed by the equation:

$$R = \frac{2 S^0 + 3 S^=}{\sum K} \quad (4)$$

where S^0 , $S^=$ and K refer to the mols of zero-valent sulfur, sulfur with a valance of -2, and total mols of K in the feed solution associated with the compounds KHS, K_2S_x , KHCO_3 and K_2CO_3 .

The above ratio R is termed the "acceptability ratio." When R equals 1, reaction (3) would proceed quantitatively to produce pure thio-sulfate. When R is greater than 1, a surplus of sulfur is present in the feed solution and H_2S may be evolved into the stack. In practice R should be close to but below 1 to maintain an excess of sulfite to help drive reaction (1) to completion.

Lower values of R are undesirable as this permits the concentrations of sulfite and bisulfite ion in the circulating scrub solution to increase. The result is a decrease in the absorption of SO_2 and an increase in sulfate formation as a result of the oxidation reaction:

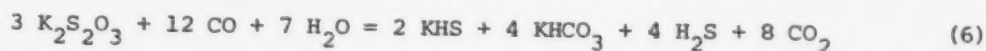


The sulfate yield in the process is, however, quite low and is easily kept to about 1 mol % or less of the SO_2 absorbed. This is a consequence of the low sulfite concentration maintained in the process, and the fact that concentrated solutions of thiosulfate strongly inhibit the oxidation reaction (5). The low sulfate yield in the revised process is one of the principal advantages. The K_2SO_4 also is readily saleable.

Because of the high solubility of $\text{K}_2\text{S}_2\text{O}_3$ in water, it is possible to operate the scrubber system with a highly concentrated salt

solution. Clear solutions are handled throughout the process except at the point of sulfate removal. Particularly important is the fact that no deposition of solids or scaling takes place in the scrubber.

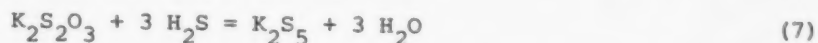
The regeneration system in the Consol process is illustrated schematically in Figure 2. The basic reaction is the noncatalytic reduction of thiosulfate with a carbon monoxide-rich gas. The reaction may be written as follows:



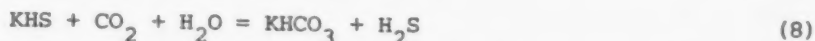
The optimum temperature for the reaction from the practical point of view is in the neighborhood of 450°F. Total pressures in the range of 500-1000 psig are suitable. Typical operating conditions for the various process blocks are shown in Figure 2.

Hydrogen, in the absence of a catalyst, is inert under these conditions. Hydrogen may be utilized, if desired, by introduction of a catalyst containing metal sulfides of Group VI and/or Group VIII supported on active carbon as reported in 1973 by Urban and Alpert⁽³⁾ and by Urban⁽⁴⁾. The use of a catalyst was tested, but was rejected to maintain simplicity of the system.

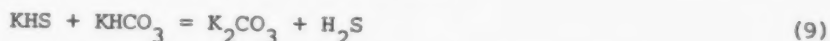
Some polysulfides are formed during regeneration. They probably result from reduction of $\text{K}_2\text{S}_2\text{O}_3$ with H_2S :



The ratio of KHS to KHCO_3 in the reduction product is dictated by establishment of equilibrium in the reaction:



The acceptability ratio thus may be controlled by the amount of CO_2 in the reducing gas. Operation of the pilot regenerator was normally carried out so that the acceptability ratio of the reactor product was above 1.0. The final adjustment of acceptability ratio to the desired value of about 0.95 was achieved in the flash drum (cf. Figure 2). Here the acceptability ratio is reduced by the decomposition reaction,



Simultaneously CO_2 is released by the decomposition reaction,

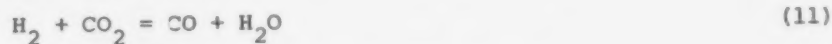


The release of CO_2 does not affect the acceptability ratio, but it does convert slightly soluble KHCO_3 into more soluble K_2CO_3 .

The off-gas from the regenerator contains unreacted CO , H_2 , CO_2 and H_2S . The H_2S is selectively removed, after cooling and condensation of the steam, by scrubbing with a polar organic solvent. Several proprietary processes are available for this service. The absorbed

H₂S-CO₂ gases are released from the solvent in its regeneration. These are combined with the H₂S-CO₂ gas released in the flash drum and sent to a Claus plant where the H₂S is converted to sulfur. The Claus tail gases are incinerated with a portion of the scrubbed regenerator offgas to provide hot flue gases for direct reheating of the scrubbed stack gas.

The major portion of the cleaned regenerator offgas is recycled through an oxygen-fired, partial-oxidation unit. No steam is added to the unit and hydrogen in the recycle gas is converted to CO by reverse water-gas shift:



EXPERIMENTAL

The entire Library scrubbing unit, i.e., venturi, scrubber and reaction drum, was constructed of type 316 stainless steel. The bottom section of the scrubbing tower served as a cyclone separator to remove the venturi water. A chevron-type mist eliminator was used above the separator to prevent water droplets from entering the packed section.

The scrubbing tower was 20 inches ID and contained a 42 inch depth of No. 1 Intalox packing in the form of polypropylene saddles. A distributor was used to supply an even flow of the recycle liquid over the top of the packing. A York mesh-type demister was used above the packing.

Hot flue gas was supplied to the Library unit from a packaged boiler fired with No. 2 fuel oil. A forced-draft fan was used to drive the flue gas through the scrubbing unit. Sulfur dioxide was metered into the gas to achieve concentrations similar to that in the coal-fired units. Provisions were also made to feed flue dust into the gas prior to the venturi.

The Cromby pilot plant was constructed in a similar manner. The flue gases were taken from the output of a 160 MW, coal-fired boiler as a side stream and a separate forced-draft fan was used to drive the gases through the unit. The venturi was constructed of type 316 stainless steel.

The scrubbing tower was 8 ft ID and, in contrast to the Library unit, was constructed of rubber-lined carbon steel. The lower section again was used as a cyclonic separator above which was a chevron-type mist eliminator. The packed section was 5 ft high. The packing initially used was No. 3 Intalox polypropylene saddles. A weir-trough liquid distributor was used, but distribution between the two weirs proved to be unequal. After Run 2, the packing was changed to No. 2 Intalox plastic saddles, and an improved liquid distributor was installed to ensure equal flow to the weirs. The initial configuration also used a York mesh, style 931, teflon mist eliminator at the top of the tower. The reaction drum and all the piping for the pump-around circuits were constructed of rubber-lined carbon steel.

The regeneration pilot unit is shown schematically in Figure 3. The regeneration vessel itself was a mechanically-agitated, gas sparged unit equipped with a Hastelloy liner for protection against stress corrosion cracking due to chloride ion contaminants in the feed. Hot liquid piping also consisted of Hastelloy tubing. All other tubing and equipment such as the flash drum were constructed of 316 stainless steel.

The agitation was effected by a six-bladed turbine impeller, 8.5 inches OD, driven through a mechanical seal by a variable-speed drive, generally at 330 rpm. The rate of absorption of CO was found to vary with the 1.8 power of the rpm, which is similar to the value of 2.0 found by Yoshida et al in 1960⁽⁵⁾.

The liquid pool in the regenerator was 15 inches ID x 15 inches high. Level was controlled by an overflow weir through which the regeneration product flowed into the surge pot below the regenerator vessel.

Integrated operation with the scrubber and regenerator was carried out by continuous circulation of salt between the two units. The regenerator and scrubber feed tanks provided surge capacity. The closed-loop operation was conducted continuously for a period of ten days. This corresponds to 12 turnovers of the inventory.

DISCUSSION OF RESULTS

Scrubbing

At Cromby, a series of tests with water scrubbing was run initially to check the mechanical components and the operation of the venturi. The venturi pressure drop was 150% of the design value even with the variable plug fully extended. All tests were therefore run with higher than desired pressure drop. With a flue gas input of 16,000 SCFM, the venturi operated with a pressure drop of 11 to 13 inches of water. The inlet dust loading was 0.22 grains/SCF and the outlet 0.01 grains/SCF for 95% dust removal. Eighty percent of the removed particulates were within the range of 3 to 10 microns. No measurable particulates were removed in the scrubbing loop.

The results of the SO₂ scrubbing tests are given in Table 1. Tables 2 and 3 give the composition of the feed and product solutions and gas, respectively.

The first test, CS-2, was carried out with the larger size, No. 3 saddles. It was a continuous ten-day run. No increase in pressure drop over the packing was observed during this run. The York demister showed a very slight increase in pressure drop for the first seven days and thereafter it went up sharply due to collection of fly ash. It was necessary after this to periodically back-flush the demister with water every 22 hours for a period of 45 to 60 seconds. The back flushing temporarily restored the pressure drop to its original value.

Tests showed that at the 20,000 ACFM gas rate used in this run, less than 0.01% of the potassium in the fresh feed solution would exit the stack without a mist eliminator.

Average absorption of SO_2 was relatively low in this run, i.e., 88%. It was found, however, that proper control could be maintained, and the percent removal of SO_2 held constant during wide swings of as much as a factor of 4 in the SO_2 concentration of the entering flue gas. Inspection of the packing after the run showed it to be clear with only an insignificant film of salt on the packing.

For subsequent runs the No. 3 Intalox packing was replaced by No. 2 packing. A new liquid distributor and pumps of higher capacity also were installed. The mist eliminator at the top of the scrubber was replaced by the Heil blade mist eliminator from the top of the cyclone separator. Runs CS-3A, 3B and 4 were carried out in sequence for a period of continuous operation of 6.5 days. During this period, no increase in pressure drop over the packing was observed. The mist eliminator remained clean and no appreciable foaming or carryover of scrubbing solution was noted. The only difference between Runs CS-3A and 3B was the higher liquid circulation rate employed in the latter run.

The use of the improved distributor and the smaller packing increased SO_2 absorption from 88.0 to 96.2%. Increasing the liquid circulation rate in Run CS-3B raised the absorption of SO_2 to 98%. The use of the higher gas rate increased the SO_2 absorption to 99%, but only at the expense of a considerable increase in pressure drop.

The sulfate formation was small throughout all of these runs and averaged about 1% of the SO_2 absorbed. No appreciable NO absorption could be detected within the precision of measurement. Mass transfer coefficients for SO_2 absorption were in the same range reported by Johnstone and Singh in 1937⁽⁶⁾.

The rubber lining in all the vessels was in good shape after this operation. Corrosion information was also collected via strips and spools in the system. Based on these short-term results (518 hours), the choice of materials would be among rubber-lined carbon steel, type 316 stainless steel, and fiberglass reinforced pipe.

Closed-Loop Operations

The closed-loop run was conducted over a steady operating period of ten days. During this period, the pressure drop through scrubber and demister remained quite constant. A mesh-type demister was used in the Library scrubber and, in contrast to the experience at Cromby, no plugging problem was encountered. It is concluded from this and other evidence that the plugging of the Cromby demister was due primarily to the entrapment of fly ash.

The sulfate yield averaged slightly less than 1 mol % of the SO_2 absorbed. Only a fraction of the sulfate was removed by the line filters²

in the scrubber product line (cf. Figure 1) or the regenerated feed system (cf. Figure 2). The major portion of the sulfate settled out in the regenerated product tank. It is at this point in the system that the sulfate is least soluble. Recent work has demonstrated continuous rapid removal of this sulfate after the flash drum via low-pressure filtration.

The only materials added or removed during the run were water and a small amount of K_2CO_3 added to make up for the K_2SO_4 removed. In a commercial process, no dilution water need be added except to humidify the gas, since the condensate liquor would be returned to the product salts (cf. Figure 2).

The initial inventory was turned over twelve times in the course of this run. No foreign materials accumulated in the product. The compositions of all the feed streams, their rates, temperatures and pressures are given in Table 4. The stream numbers correspond to those given in Figures 1 and 3. The figures given in Table 4 are those midway through the operation, i.e., after five days. Sulfur absorption was high throughout this run and averaged about 99%.

Potassium formate is one of the components of the product but is not in reality a foreign material. The amount present is controlled, other conditions being constant, by the percent conversion of the thiosulfate. The higher the conversion, the higher is the formate content of the product. The formate content of the regenerator product shown in Table 4 was, for example, 4 wt. % and the thiosulfate conversion was 95 wt. %. Five days later, at the end of the run, the formate concentration was reduced to 1.7 wt. % when the thiosulfate conversion was decreased to 88 wt. %.

PROCESS ECONOMICS

A cost estimate based on an engineering study for a specific site is shown in Table 5. The scrubbing section is designed to handle the full output from a 200 MW unit with a heat rate of 9,000 Btu/KWH and 35% excess air in the stack gas to be scrubbed. The regeneration section provides the capacity to handle coal with up to 3.5 wt. % sulfur (at 12,000 Btu/lb) when the heat rate is 9,000 Btu/KWH and the average load factor of the utility is 80%. The overall sulfur removal is 93% after the incinerated Claus tail gas has been added to the scrubbed stack gas.

The costs do not include charges for venturis and fly ash removal. Retrofit costs are included. The costs were developed for 1977 startup at a time when the rate of inflation was quite high. The investment estimates correspond essentially to a Chemical Engineering Plant Cost Index of 200. The operating costs also reflect estimates for 1977 startup. Sufficient details have been given in Table 5 to adjust the investment and operating costs to other bases as desired.

The engineering study also may be used to estimate the cost at a new 1000 MW coal-fired power station. On the same basis, i.e., 1977 startup and firing 3.5% sulfur coal, the estimated investment and operating costs are 70 \$/KW and 4.1 mills/KWH, respectively.

ACKNOWLEDGMENT

Appreciation is expressed to the utility companies who provided a large part of the funding for this work. These are: Allegheny Power, Consumers Power, Detroit Edison, Niagara-Mohawk, Ontario Hydro and Philadelphia Electric. Appreciation is also expressed to C. Itoh & Company, Inc., for their financial contribution to the work reported here.

Appreciation is also expressed to the Consolidation Coal Company Management for their support of this work and their permission to publish the results.

A large number of engineers and chemists participated in this project and the success of the project was largely due to their efforts. Specifically noteworthy were the contributions by M. D. Kulik, E. B. Klunder, P. J. Dudt, W. E. McKinstry, and N. J. Mazzocco. The cooperative spirit of George Kotnick, J. A. Gille, E. G. Boyer, Jr., and M. W. Moore of the Philadelphia Electric Company during the work at Cromby Station was deeply appreciated.

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Table 1, SUMMARY OF CONDITIONS AND RESULTS
CROMBY SCRUBBING TESTS

Run Number	CS-2	CS-3A	CS-3B	CS-4
Packing Size	No. 3	← No. 2 →		
Flue gas entering venturi, ACFM	20,900	21,100	21,300	31,900
Flue gas leaving scrubber, ACFM	18,200	18,200	18,400	28,500
Liquid recirculation rate, gpm	205	190	250	255
Length of run, hours	240	36	24	94
Superficial gas velocity in scrubber, ft/sec.	6.0	6.0	6.1	9.5
<u>Temperature, °F</u>				
Flue gas entering	300	310	310	317
Gas from venturi	128	136	136	132
Gas from stack	130	138	138	140
Liquid to packing	146	150	151	157
Liquid from packing	142	148	149	140
<u>Pressure Drop, Inches of Water</u>				
Over venturi	11	11	12	25
Over packing	0.5	1.2	1.3	5.0
Total	22	15	16	38
pH of scrubber effluent	7.5	7.4	7.6	6.9
SO ₂ absorption, %	88.0	96.2	98.0	99.1
Mol % of SO ₂ absorbed producing sulfate	0.9	1.3	1.4	1.0
Calculated value, K_a , lb mol/hr ft ³ atm	21	33	40	74

Table 2, COMPOSITION OF FEED AND PRODUCT
SOLUTIONS FROM CROMBY PILOT OPERATION

Run Number	CS-2	CS-3A	CS-3B	CS-4
<u>Average Feed Composition, Wt.%</u>				
KHS	15.5	15.3	15.4	15.4
K ₂ CO ₃	31.9	32.3	32.5	32.3
Acceptability Ratio	0.95	0.94	0.93	0.94
<u>Product Composition, Wt.%</u>				
K ₂ S ₂ O ₃	54.20	54.60	55.60	32.50
KHSO ₃	1.34	1.20	1.33	1.54
K ₂ SO ₄	0.66	0.92	1.00	0.42
K ₂ CO ₃	0.2	0.2	-	0.1
Fly Ash	-	-	-	0.008
Total salts (by drying), Wt.%	57.6	57.8	59.5	35.3
<u>Distribution of Sulfur, Mol % of absorbed SO₂</u>				
K ₂ S ₂ O ₃	96.2	96.2	95.9	93.7
KHSO ₃	2.8	2.5	2.7	5.3
K ₂ SO ₄	0.96	1.33	1.40	0.99

Table 3, FLUE GAS ANALYSES
CROMBY PILOT OPERATION

Run Number	CS-2		CS-4	
	Intake	Stack	Intake	Stack
<u>Dry Gas Composition, Vol.%</u>				
CO ₂	14.1	14.2	14.5	14.5
O ₂	4.1	4.2	4.3	4.3
N ₂	80.5	80.6	80.2	80.2
Argon	1.0	1.0	1.0	1.0
SO ₂ , ppm	2975	337	2010	18
<u>Wet Gas</u>				
Vol.% H ₂ O	-	-	6.7	14.6

Table 4, OPERATING CONDITIONS AND STREAM
COMPOSITIONS, CLOSED LOOP OPERATION

Gas Stream No.	Scrubbing Section		Regeneration Section						
	1	3	16	17	18				
Flow, SCFH	45,000	47,600	430	704	148				
Temperature, °F	350	131	403	220	219				
Pressure, psig	0.7	0	595	595	26				
Gas velocity, ft/sec	-	7.3	-	-	-				
Composition, Vol.%									
CO	0.0	0.0	792	7.4	0.0				
H ₂	-	-	0.3	0.2	8.2				
CO ₂	12.0	11.3	19.9	39.3	8.2				
O ₂	3.3	3.1	0.0	0.0	0.0				
H ₂ S	0.0	0.0	0.0	14.1	8.8				
SO ₂ , ppm	2200	15	0.0	0.0	0.0				
N ₂ + Argon	74.5	69.1	0.6	4.7	24.2				
H ₂ O	10.0	16.5	0.0	34.3	58.6				
% SO ₂ Removal	← 99.5 →								
Liquid Stream No.	7	8	9	10	11	13	14	15	19
Flow, gal/hr	648	648	10.6	-	-	-	-	-	-
Flow, lb/hr	-	-	126	-	123	40	105	28	105
Temperature, °F	144	140	149	70	144	70	150	-	-
pH	7.4	6.8	-	-	7.4	-	-	-	-
Composition, Wt.%									
H ₂ O	49.7	-	57.8	-	49.7	100	51.5	100	57.7
K ₂ S ₂ O ₃	41.5	-	1.8	-	41.5	-	39.7	-	2.2
KOOCH	5.7	-	4.6	-	5.7	-	6.0	-	4.0
KHSO ₃	0.9	-	0.0	-	0.9	-	0.8	-	0.0
KHS	0.0	-	7.7	-	0.0	-	0.0	-	6.9
K ₂ SO ₄	0.8	-	0.4	-	0.8	-	0.8	-	0.9
K ₂ CO ₃	1.4	-	9.2	47	1.4	-	1.2	-	10.1
KHCO ₃	0.0	-	15.5	-	0.0	-	0.0	-	14.5
K ₂ S ₂	0.0	-	3.0	-	0.0	-	0.0	-	3.7
Acceptability Ratio	-	-	0.97	-	-	-	-	-	0.97
Absorbed Sulfur									
Converted to	0.95								
Sulfate, mol %									

Table 5, ESTIMATED COSTS FOR 200 MW PROTOTYPE, 1977 START-UP

<u>Investment Summary</u>		<u>MM\$</u>		
Scrubbing and reheat		7.1		
K ₂ SO ₄ Recovery		0.5		
Regeneration, including oxygen plant, CO generation, acid gas separation and Claus plant		14.3		
Support facilities, including storage and boiler feed water, cooling water, process water, and waste water systems		<u>2.8</u>		
Total		24.7		
<u>Operating Costs</u>	<u>Annual Quantity</u>	<u>Rate</u>	<u>Annual Costs, MM\$/Yr</u>	<u>Mills KWH</u>
Operating Labor, incl.				
Benefits	45,990 hrs	\$10.13/hr	0.466	
Supervision, incl. Benefits	8,760 hrs	\$10.93/hr	0.096	
Ind. O.H. & Admin., Incl.				
Benefits	(55% of above)		0.309	
Electricity	22,118 MWH	25\$/MWH	0.553	
High-Sulfur Fuel Oil	721,000 MM Btu	3\$/MM Btu	2.163	
KOH	898 Tons	355.60\$/ton	0.319	
Claus Catalyst	13.9 Tons	200\$/ton	0.003	
Misc. other Chemicals	-	-	0.025	
Maint. & Misc. Supplies	(5% of \$24.7 MM)		1.235	
Insurance	(0.175% of \$24.7 MM)		0.043	
Int. on Working Capital	(10% of \$1.43 MM)		<u>0.143</u>	
Sub-Total			5.355	<u>3.82</u>
Capital Charges	(16% of \$24.7 MM)		3.952	2.82
Sub-Total			<u>9.307</u>	<u>6.64</u>
Credits:				
Sulfur	16,013 LT	25\$/LT	-0.400	
K ₂ SO ₄	982 Tons	42.50\$/ton	<u>-0.042</u>	
Sub-Total, Credits			-0.442	<u>-0.32</u>
Net Total			8.865	6.32

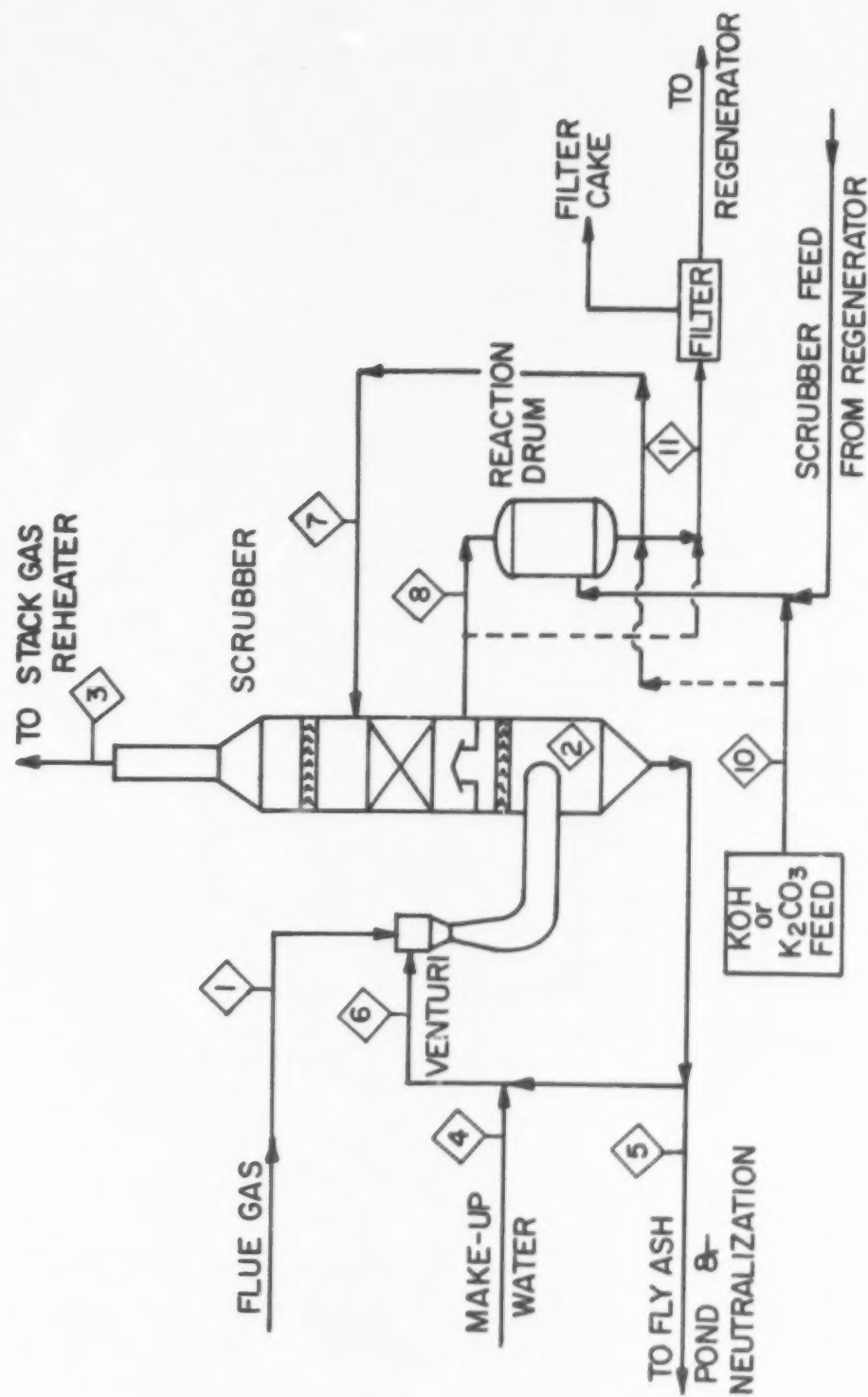


Figure 1 Schematic flow diagram, scrubbing section.

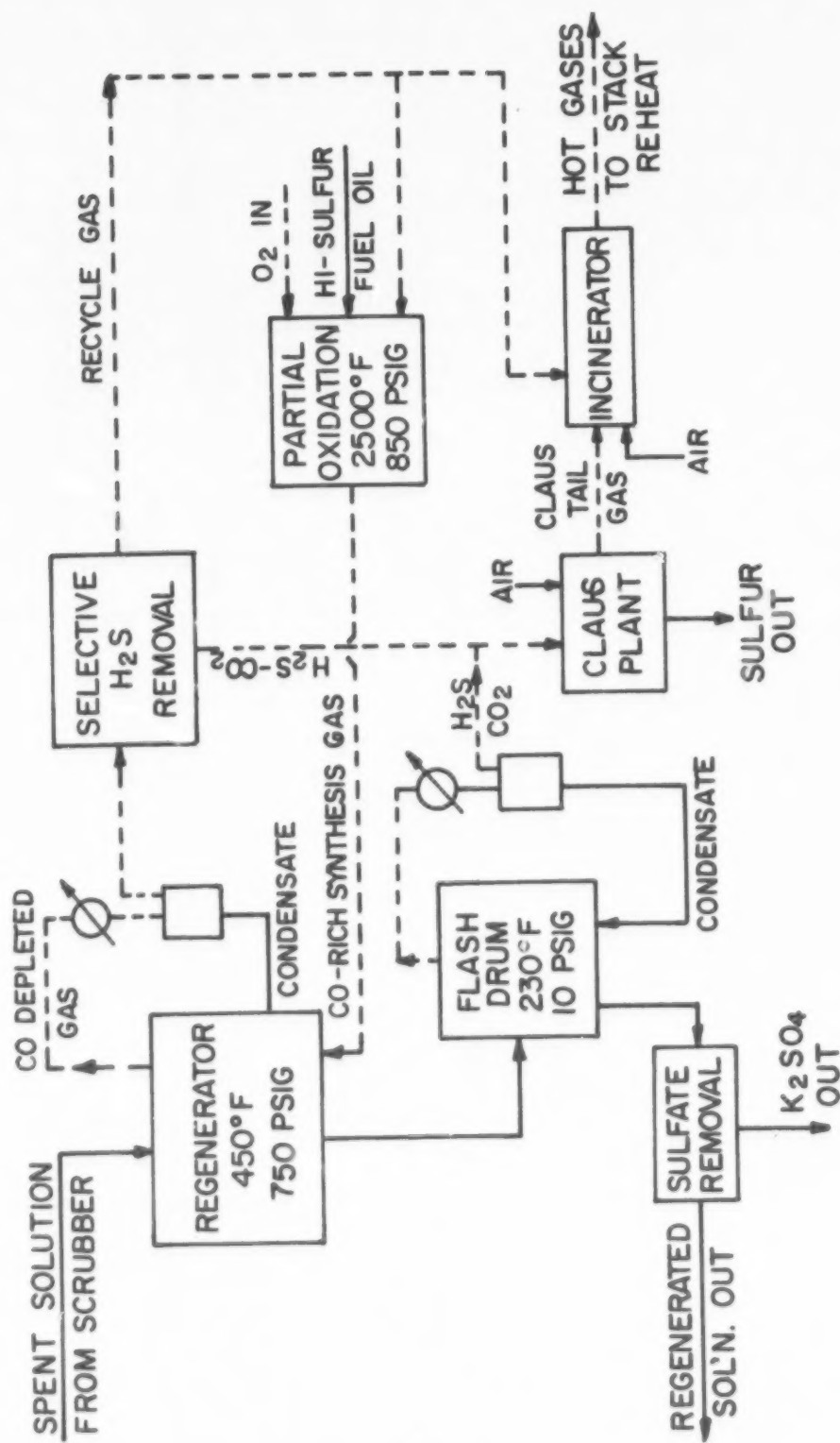


Figure 2 Block diagram, commercial regeneration process.

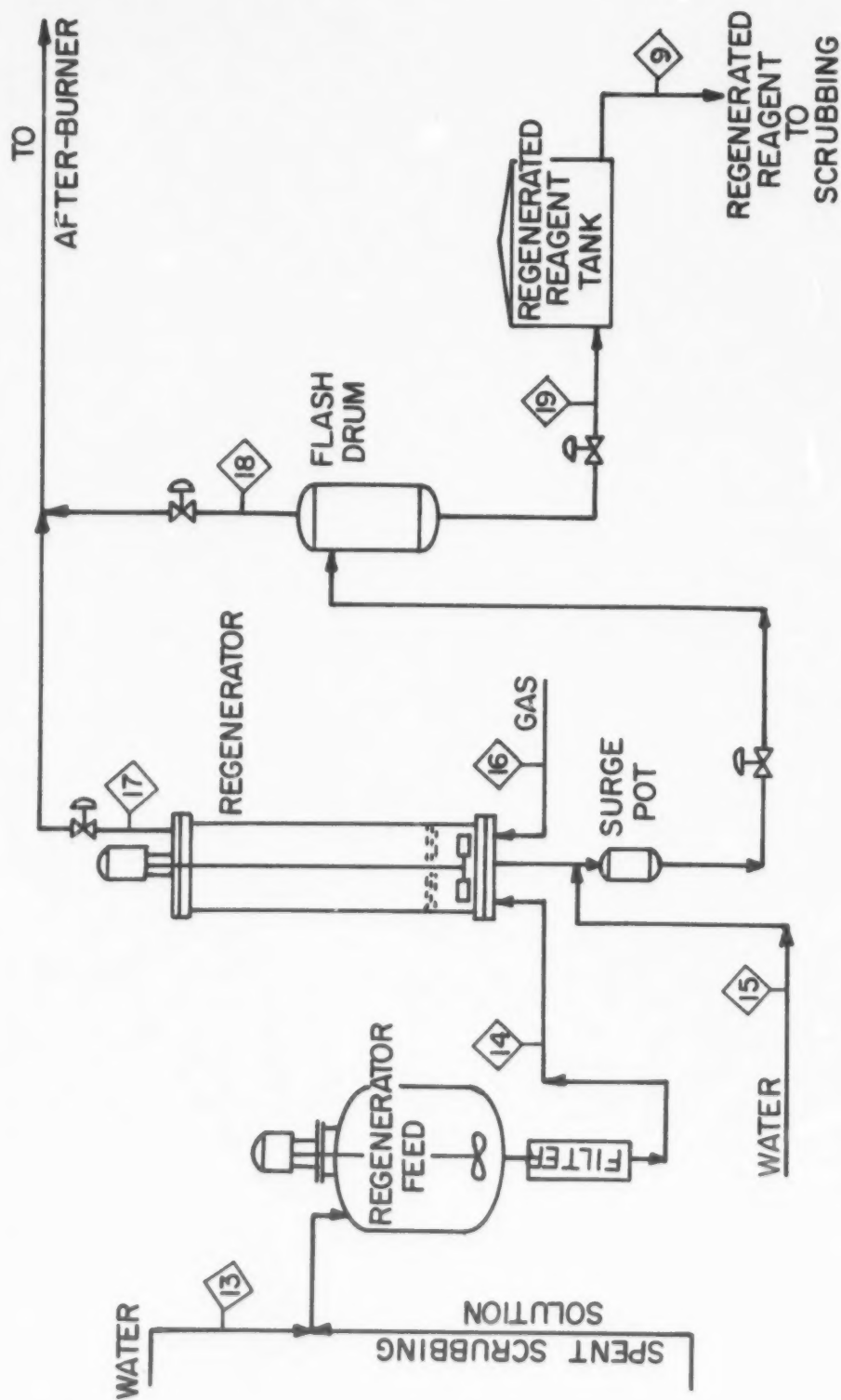


Figure 3 Schematic flow diagram, pilot regeneration.

UNPRESENTED PAPERS

INFORMATION TRANSFER PROGRAM

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INFORMATION TRANSFER PROGRAM

1.0 INTRODUCTION

In September 1975, the Process Technology Branch of the Industrial Environmental Research Laboratory/RTP, U.S. Environmental Protection Agency, contracted with PEDCo-Environmental Specialists, Inc. and Radian Corporation to develop an Information Transfer Program related to air pollution control technology. This program would establish a method for effectively disseminating data developed, at least in part, by IERL/RTP research programs. The program would be sufficiently comprehensive to address control of potential water and solid waste impacts resulting from use of air pollution control technologies.

Since the Process Technology Branch is responsible for research in the area of flue gas desulfurization (FGD), this program was initiated with FGD related information transfer products. If this program is successful, it may be expanded to cover other pollutants, control techniques and industries. Potential pollutants to be addressed include particulates, nitrogen oxides, hydrocarbons, and carbon monoxide. Other sulfur dioxide control strategies include

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clean fuels (physically and chemically cleaned coal), process modifications (e.g., fluidized bed combustion), and fuel conversion (coal gasification and liquefaction).

2.0 PROGRAM APPROACH

To assess the need for the Information Transfer Program, the following three tasks were undertaken, using FGD as the evaluation vehicle.

Assess the FGD Data Base - Radian Corporation examined the data at IERL/RTP and other sources to determine the extent of information available for the transfer program.

Prepare Examples of Program Outputs - Both Radian and PEDCo prepared examples of potential program outputs. An audio-visual presentation was prepared to explain the program to potential users. Radian was responsible for the summary reports, newsletters, direct contact meetings and symposia outputs, while PEDCo-Environmental was responsible for example products related to FGD system data books and FGD system evaluation procedures.

Assess the Information Needs of Prospective Users - When the proposed program was first formulated, the following groups were identified as potential users:

- ° EPA Regional and state/local environmental agencies
- ° Electric utilities
- ° Environmental consulting firms
- ° Architectural and engineering firms
- ° Selected industries with potential SO₂ control needs, such as metal processing, paper and allied products, petroleum refining and related products, sulfuric acid production, and coal mining.

An audio-visual program was presented at the ten EPA Regional Offices to determine, first, their overall interest in the program and then specifically, their recommendations for ITP outputs. Presently, the Information Transfer Program is being explained to representative electric utilities, again to determine whether there is sufficient interest and need, and to define the content and format of ITP products. A final phase of this program involves presentation to selected industrial users.

3.0 POTENTIAL ITP PRODUCTS

Various potential "products" of the ITP were identified for the various "user" categories described above. These products are briefly described below.

Summary or Capsule Reports - Reports will be written to cover specific aspects of an SO_x control strategy. Capsule reports would address first and second generation FGD processes. Each report would include:

- ° Process description
- ° Design considerations
- ° Status of development
- ° Raw material and utility requirements
- ° Costs
- ° Land requirements
- ° Environmental considerations

Newsletters - Newsletters would present information not contained in current commercial or governmental newsletters, such as:

- ° Status reports on control technology. This would include new developments in technology or improved methods for utilizing existing technology.
- ° A series of abstracts covering recently published reports on selected subject areas.
- ° A list of knowledgeable contacts in the field of sulfur dioxide control technology.

Symposia and Direct Contact Meetings - Two levels of meetings are being considered.

- ° National and regional symposia - This FGD symposium is a good example of an effective information transfer symposia related to a specific subject area. Other symposia could cover such areas as coal cleaning, low sulfur coal, coal liquefaction, and coal gasification, and be conducted on a regional or national basis.
- ° Direct contact meetings - Meetings would be held in workshop format. This would provide close interaction between individuals requiring information on SO_x control and experts who can provide such information.

Data Books - Data books would be prepared for such developed FGD processes such as lime and limestone. Data limitations prevent the preparation of detailed data books for other processes. The purposes of the data book are:

- ° Provide comprehensive, up to date information on existing FGD systems in a format suitable for use by design engineers and those evaluating proposed FGD system designs.
- ° Provide data to aid in the selection and evaluation of FGD systems on a site specific basis.
- ° Provide a format for periodic updating of process information.

The data books would be technically oriented, addressing a user audience involved in the design, operation, and evaluation of FGD systems.

A summary of the proposed outline for the data books follows:

1. Process Description - A detailed process analysis will be presented. Flow sheets and material and energy balances would be presented for "typical" installations.
2. Process Data - Data required to evaluate a process will be identified. Data from operating systems will be presented along with the results of tests conducted by pump manufacturers, etc.
3. Process Design - Design data will address such areas as velocities, L/G ratios, efficiencies, pressure drops, stoichiometric ratios, and solids content for various system operating modes.
4. Project Design - Installation schedules will be provided for single and multiple module FGD systems. Information on space requirements and retrofit layouts will be provided.
5. Process Operation - Manpower requirements, including skill levels, for the maintenance and operation of an FGD system will be identified. Information on potential FGD system operating problems will be presented.
6. Process Cost Data - Calculational procedures will be presented to permit the user to estimate the cost of a proposed FGD system or to analyze costs submitted by FGD system vendors. The user will then be able to obtain relative cost estimates for different design and operating conditions.
7. Case Histories of Process Applications - Case histories will be presented for selected FGD installations. Problems and solutions encountered at these FGD installations will be described.

FGD Evaluation Procedures - Development of the following procedures is being considered to aid in the evaluation of FGD systems:

- ° Procedure for FGD system reliability evaluation.
- ° Procedure for an interprocess comparison/selection of an FGD system on a site specific basis.
- ° Procedure for FGD system cost/reliability evaluation.

Several versions of each evaluation procedure will be prepared to accommodate multiple users and different desired levels of complexity. The procedures are described below:

- ° Reliability Evaluation Procedure - This model will aid in evaluating the reliability of flue gas desulfurization and particulate control systems. This simple procedure will permit estimation of the percentage of down-time for the control system. Since reliability data are not always available, the procedure will contain data that can be substituted for actual system data as a first level approximation. The procedure can be performed manually in two or three hours.
- ° Interprocess Comparison/Selection Procedure - This procedure will aid in the selection and comparison of FGD systems. The procedure will determine the annualized operating and capital costs for different FGD processes at specific sites. Site specific constraints such as retrofit difficulty, sludge disposal, by-product marketability, fuel penalties, and process complexity would be factored into these procedures. The procedure will not only aid in determining the lowest capital cost system for a specific site, but the lowest cost system over the life of the installation.
- ° Cost/Reliability Evaluation Procedure - This procedure will aid in the evaluation of various intraprocess alternatives. Cost/benefit analysis will be performed to determine the impact of spare components on total system cost and reliability. This procedure will be fairly sophisticated,

require good FGD component reliability data and be computerized to be properly utilized. Figures 1 through 5 present system design scenarios illustrating the impact of component sparing and increasing component reliability on process operability and cost.

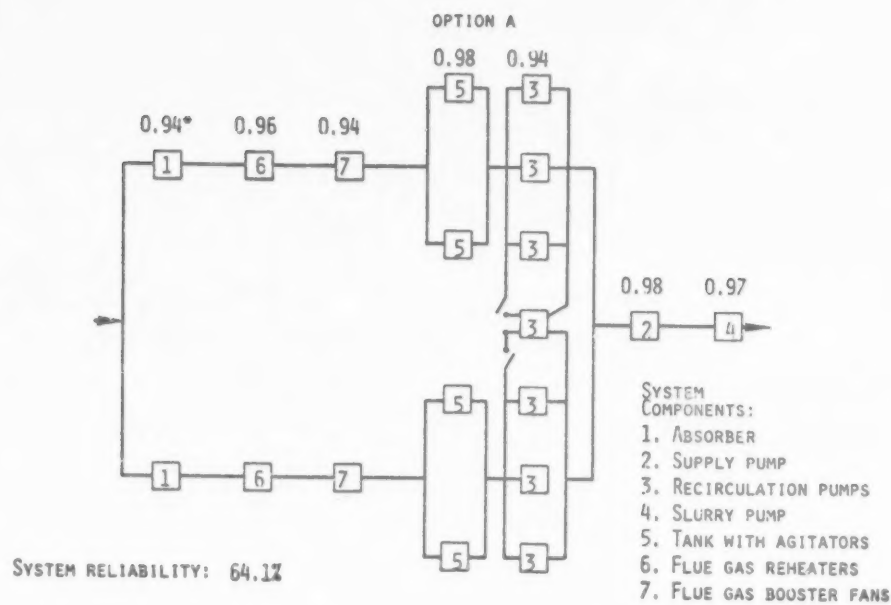
Figure 1 presents a two module scrubber on a 300 MW boiler with a single spare absorber recirculation pump for both modules (system reliability is 64.1 percent). Figure 2 shows the addition of a second spare recirculation pump; reliability has improved to 65.6 percent. Figure 3 illustrates the sparing of additional pumps in the system and the subsequent improvement in reliability. Figures 4 and 5 illustrate two methods for obtaining the same system reliability. In Figure 4, the reliability of the component has been improved by design changes; fans, absorbers, and reheater reliability can be improved by changes such as use of forced draft fans, simpler absorber internals, and moving reheaters out of the flue gas stream). Although these changes raise costs, they are still more economical than adding a spare absorber as shown in Figure 5. Table 1 summarizes the reliability, capital costs, annual costs, and expected costs, and untreated gas percentages for Figures 1 through 5.

4.0 BENEFITS FROM THE INFORMATION TRANSFER PROGRAM

Potential benefits of the various ITP products are listed by user group.

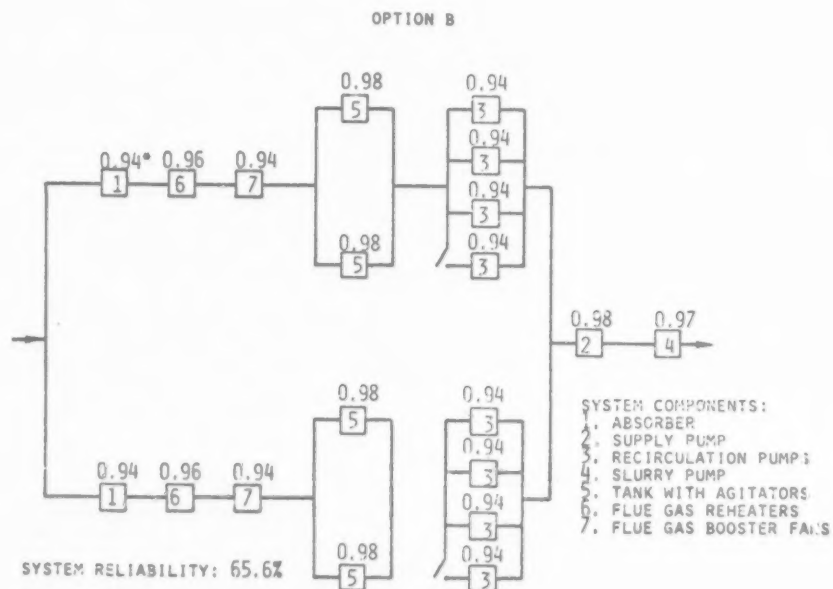
Regional and Local Environmental Agencies

- ° Provides effective training tools.
- ° Presents technical and cost data on FGD systems in a consistent format.



* COMPONENT RELIABILITY

Figure 1. FGC system reliability evaluation.



*COMPONENT RELIABILITY

*HYPOTHETICAL DATA

Figure 2. FGC system reliability evaluation.

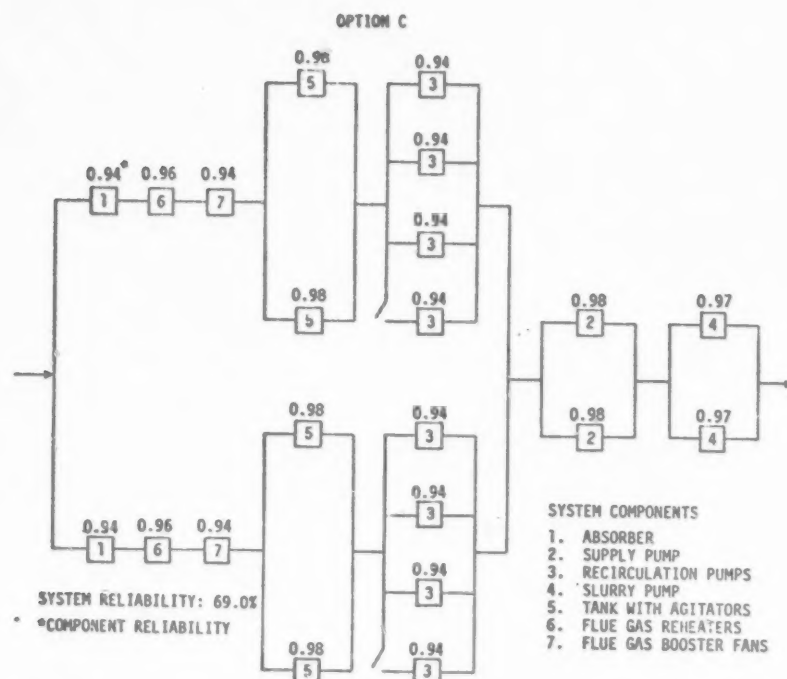


Figure 3. FGC system reliability evaluation.

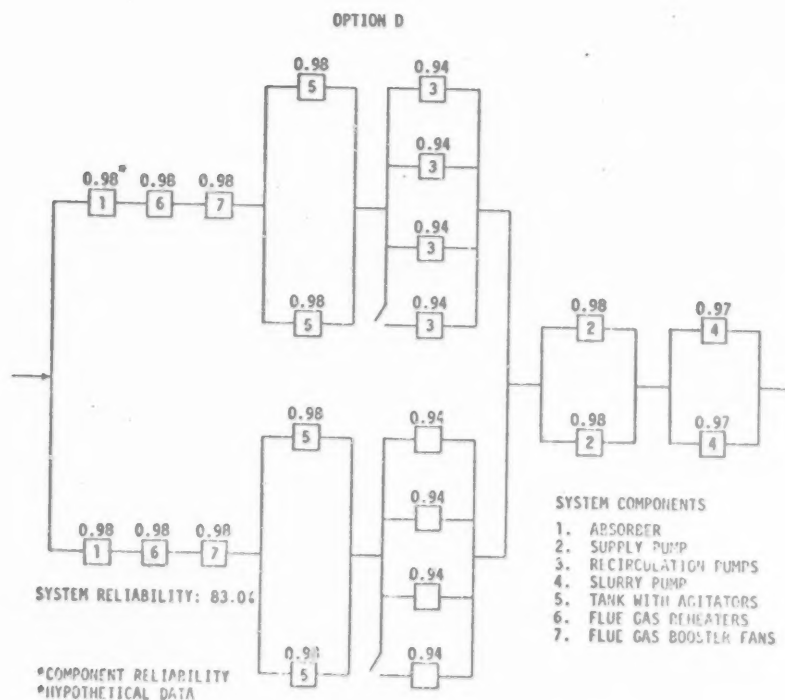
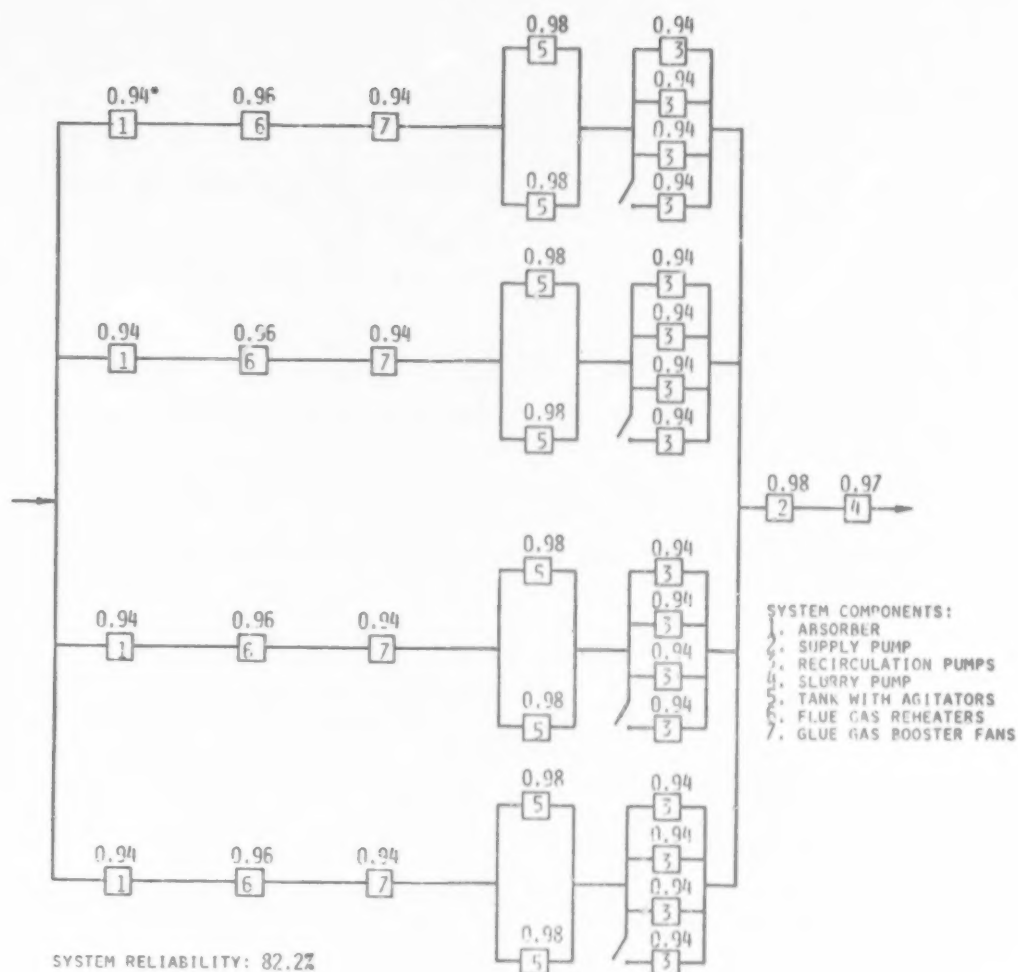


Figure 4. FGC system reliability evaluation

OPTION E



*COMPONENT RELIABILITY

*HYPOTHETICAL DATA.

Figure 5. FGC system reliability evaluation.

Table 1. ESTIMATED CAPITAL AND OPERATING COSTS

CONTROL OPTION	GAS FLOW RATE ACFM	CAPITAL COST, \$/KW	ANNUAL COST, MILLS/KWH	ANTICIPATED SYSTEM RELIABILITY, %	EXPECTED COST, MILLS/KWH	PERCENT OF TIME FLUE GAS NOT TREATED
A	900,000	71.68	4.97	64.1	8.19	10.75
B	900,000	72.62	5.02	65.6	8.23	10.70
C	900,000	73.19	5.04	69.0	7.35	7.7
D	900,000	76.17	5.19	83.0	6.28	3.6
E	1,200,000	93.18	6.22	82.2	7.55	4.4

ASSUMPTIONS

1. COST OF REPLACEMENT POWER IS 3.0 MILLS/KWH.
2. REPLACEMENT POWER IS USED 100% OF THE TIME TO REPLACE UP TO 70% OF CAPACITY, WHEN ACFM = 900,000.

- ° Can be used to estimate the potential operating reliability of FGD systems.
- ° Presents data for the evaluation of control system permit applications.
- ° Provides a forum to discuss air pollution control requirements.

Utilities and Industries

- ° Permits systematic evaluation of FGD process alternatives.
- ° Aids in the selection of the optimum FGD process.
- ° Provides a basis for comparing requirements of FGD systems.
- ° Provide background documents on new processes.
- ° Permits the transfer of experience gained by solving operating problems at other installations.

Architects/Engineers and Environmental Consultants

- ° Aids in intraprocess FGD system selection.
- ° Identifies FGD process problem areas and methods to improve process reliability.
- ° Aids in preparing equipment and system specifications.
- ° Provides a forum to update and transfer process data.

CATALYTIC/WESTVACO DESULFURIZATION PROCESS
PROTOTYPE DEMONSTRATION PROGRAM

Catalytic, Inc.
Centre Square West
Philadelphia, Pa. 19102

ABSTRACT

A dry, fluidized-bed process using activated carbon for recovery of SO_x from flue gas has been developed and patented by Westvaco Corporation. The process features several improvements over other carbon-based processes, such as minimizing carbon loss normally attributable to chemical consumption and physical attrition, improving heat transfer characteristics while reducing equipment size by employing fluidized bed reactors, and generating sulfur as the sole by-product.

The technology was successfully demonstrated in an extended 20,000 CFH integral pilot run on a slipstream of an oil-fired boiler. Over 90% SO_2 removal and virtually 100% SO_3 removal was observed over a span of some 300 hours on-stream. Bright-yellow, 99.9% pure elemental sulfur was by-produced. After the test program, Westvaco selected Catalytic, Inc. as its engineering partner with direct responsibility for all facets of continuing commercialization: marketing, engineering, installation and, when appropriate, operation of the process.

Since the technology has never been demonstrated in a coal-fired situation, or when using producer gas as the chemical reductant, Catalytic included these aspects in preparing an engineering evaluation, design, cost estimate and schedule for a 30 MW (60,000 SCFM) prototype demonstration program. Catalytic's evaluation supported Westvaco's initial appraisal of process viability. Capital expenditure for the prototype installation was estimated to be \$5.9 million. An operating budget of \$1.2 million was projected for a nine-month test program. All phases of the demonstration including design, installation, operation and evaluation can be completed within a 2.5 to 3 year period.

Conceptual economics for a 500-MW installation (available on request) indicated competitiveness with other regenerable FGD processes under development. Coupled with documented technical viability, these economics strongly suggest that the Catalytic/Westvaco process merits demonstration on the prototype scale.

CATALYTIC/WESTVACO DESULFURIZATION PROCESS PROTOTYPE DEMONSTRATION PROGRAM

INTRODUCTION

"Activated carbon" is the generic term for specially processed carbonaceous substances which possess high internal surface areas and are commonly employed as adsorbents in air and water purification systems. Less exploited but equally well understood is the ability of certain grades of active carbon to adsorb and to catalyze the oxidation of sulfur dioxide to SO_3 . The sulfur trioxide thus formed is subsequently hydrolyzed to sulfuric acid which remains loosely bound to the carbon until a regenerative operation is implemented. Historically, many approaches featuring activated carbon for desulfurization have been explored. Although effectiveness for SO_x removal was usually found to be acceptable, most of the early processes had fundamental problems, some of which were:

- 1) Carbon loss due to burn-off (chemical degradation) or abrasion (attrition).
- 2) Carbon ignition hazard due to "hot-spots" in adsorber.
- 3) Sulfurous by-products, such as dilute acid, often undesirable in the U.S.

Westvaco, a major U.S. corporation and a leader in the pulp and paper industry, recognized the potential in exploring the desulfurization market for active carbon, which is a major product of their specialty chemicals group. In a conceptual development phase, Westvaco attacked the carbon loss problem by effectively eliminating chemical burn-off, thereby allowing a high quality (abrasion-resistant carbon) to be used. Consequently, adsorbent make-up requirements were stabilized at an acceptably low level. The hazard of potential spontaneous ignition of the adsorbent bed was eliminated, not only because the carbon selected for use has a high ignition temperature, but also because the fluid-bed method of gas/solid contact offers excellent heat transfer properties (eliminating hot-spots) and promotes thorough mixing of the carbon granules. Regarding by-products, Westvaco developed a unique sulfur-producing regenerative technology. Merchant-grade sulfur is potentially the most valuable and certainly the most convenient of all possible end products from a desulfurization process.

The culmination of Westvaco's preliminary laboratory and pilot work was a closed-loop, fully regenerable process comprising only three major steps -- each one taking place in a fluidized bed. The integral pilot plant (in Charleston, S.C.) treated a 20,000 CFH slipstream from an oil-fired boiler. The pilot unit was operated over a period of years to obtain fundamental data and to establish long-term operational stability. Westvaco experienced consistently satisfactory performance in removing greater than 90% of the incumbent SO_x over a period of more than twenty cycles of the carbon (greater

than 300 hours on stream). A comprehensive review of Westvaco's development program and pilot activities has previously been presented.*

Recognizing the need to convert its technological expertise into a reliably optimized process, Westvaco sought a licensee with proven competence in the engineering and construction industry, experience in clean energy technology, and established contacts in the electric utility industry. Consequently, in May, 1975 Catalytic, Inc., was granted the exclusive right to continue the technical development and assume the marketing responsibility for Westvaco's activated carbon desulfurization system.**

As the first phase of its involvement, Catalytic developed a preliminary engineering study and cost estimate for an unsited 30-megawatt (60,000 CFM) prototype scrubber to desulfurize a slipstream from a coal-fired utility boiler. Catalytic and Westvaco had agreed that the extensive pilot and bench scale programs previously implemented by Westvaco had already fulfilled their ultimate purposes. Further advancement of the technology would require a demonstration of significant scale in commercially available apparatus. In selecting the size of the prototype, overall cost must be weighed against scale-up potential and "believability". Although a 30-megawatt basis was chosen for Catalytic's study, the optimum capacity might be in the range of 10 to 40 MW.

The results of Catalytic's engineering study form the theme of this presentation. In effect, it is actually the prospectus for a proposed demonstration program featuring the Catalytic/Westvaco technology. Although this paper describes a potential demonstration in an electric utility station, it should be emphasized that the subject process is equally applicable in non-utility situations; e.g., smelters, industrial boilers, oil refineries (CO boilers), sulfuric acid plants, and others. Data presented here are easily convertible in terms familiar to various industrial plant operators.

Catalytic, Inc., before accepting the major financial responsibility for development and promotion of this process, had thoroughly reviewed its technical aspects and carefully assessed its potential marketability. As a result, Catalytic became convinced that it constitutes a significant

*Ball, F.J., et al., Westvaco Activated Carbon Process for SO_x Recovery as Elemental Sulfur, EPA Atlanta, Ga. conference (Nov. 1974). (Copies available on request to Catalytic, Inc.)

**Catalytic, Inc. a wholly-owned subsidiary of Air Products and Chemicals, Inc., is a major U.S. engineer/constructor/plant maintenance contractor. Catalytic and Air Products maintain active research and development program in gas desulfurization, coal liquefaction (SRC) and coal gasification. Further details upon request.

advancement in the state-of-the-art in stack gas desulfurization. The process clearly embodies a number of advanced features and appears to be highly competitive in capital and operating economics. Some of its outstanding features are:

- 1) Process is dry -- no aqueous waste streams are handled. Corrosion problems are minimized.
- 2) Process operates at normal stack gas temperature -- reheat is not required. Steam plumes are not formed.
- 3) Raw-material make-up is minimal. Carbon loss by chemical or physical means is effectively minimized.
- 4) Process is conceptually simple -- only three major unit steps are required between the raw flue gas and pure sulfur.
- 5) SO_3 is effectively removed together with SO_2 .
- 6) The process is modular and separable.
- 7) Elemental sulfur is the only by-product. No objectionable substances are discharged from the system. Special treatment of waste is unnecessary.
- 8) When a coal gasifier is integrated into the process scheme (as this paper illustrates), the system's only energy inputs are electricity, coal and low-pressure steam.

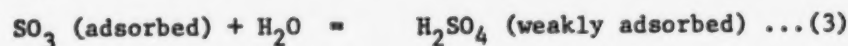
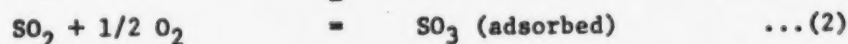
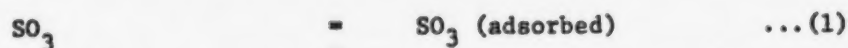
The Catalytic/Westvaco process satisfies the generally accepted criteria for an advanced, second-generation technology because it is purge-free, sulfur-producing, modular, and not dependent upon natural gas, LPG or petroleum distillates. It offers great versatility in that it can desulfurize gaseous emissions over a wide SO_x concentration range -- from several percent to practically zero. Intrinsically simple to control, the process responds rapidly and positively to changes in inlet gas composition. Turndown of fifty percent can be accomplished in a single scrubber; greater turndown can be achieved with multiple modules.

This paper presents the preliminary engineering design and associated costs for a 30-megawatt equivalent FGD system installation and test program. Its intent is to guide the reader through the steps necessary to establish viable commercial technology using Westvaco's experimental results as the starting point. Catalytic's underlying objective is to explain why the subject process merits additional investment of time and resources.

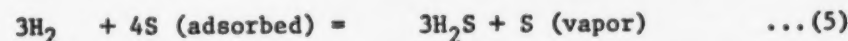
PROCESS SUMMARY AND SCHEMATIC

The Catalytic/Westvaco system is designed to convert sulfur oxides scrubbed from flue gas into merchant-grade sulfur. Activated carbon functions as the recirculating adsorbent and catalyst to promote the following principal reactions:

Adsorption:



Regeneration:



Where particulate-laden gas is to be treated, an electrostatic precipitator is normally recommended to reduce stack opacity. The Westvaco adsorption system is relatively insensitive to incumbent fly ash, but it is ineffective for particulate removal.

The adsorber is a multi-stage fluidized bed which operates in the temperature range of utility exhaust gas (about 300°F). SO_3 is removed on the bottom stage via reaction (1), and the gas is cooled slightly by partial humidification to enhance SO_2 removal in the upper stages via reactions (2) and (3). Clean gas is exhausted at temperatures above 200°F under conditions which normally do not lead to the formation of steam plumes. Since SO_x is not condensed in the gas phase, corrosion is not expected to be a problem.

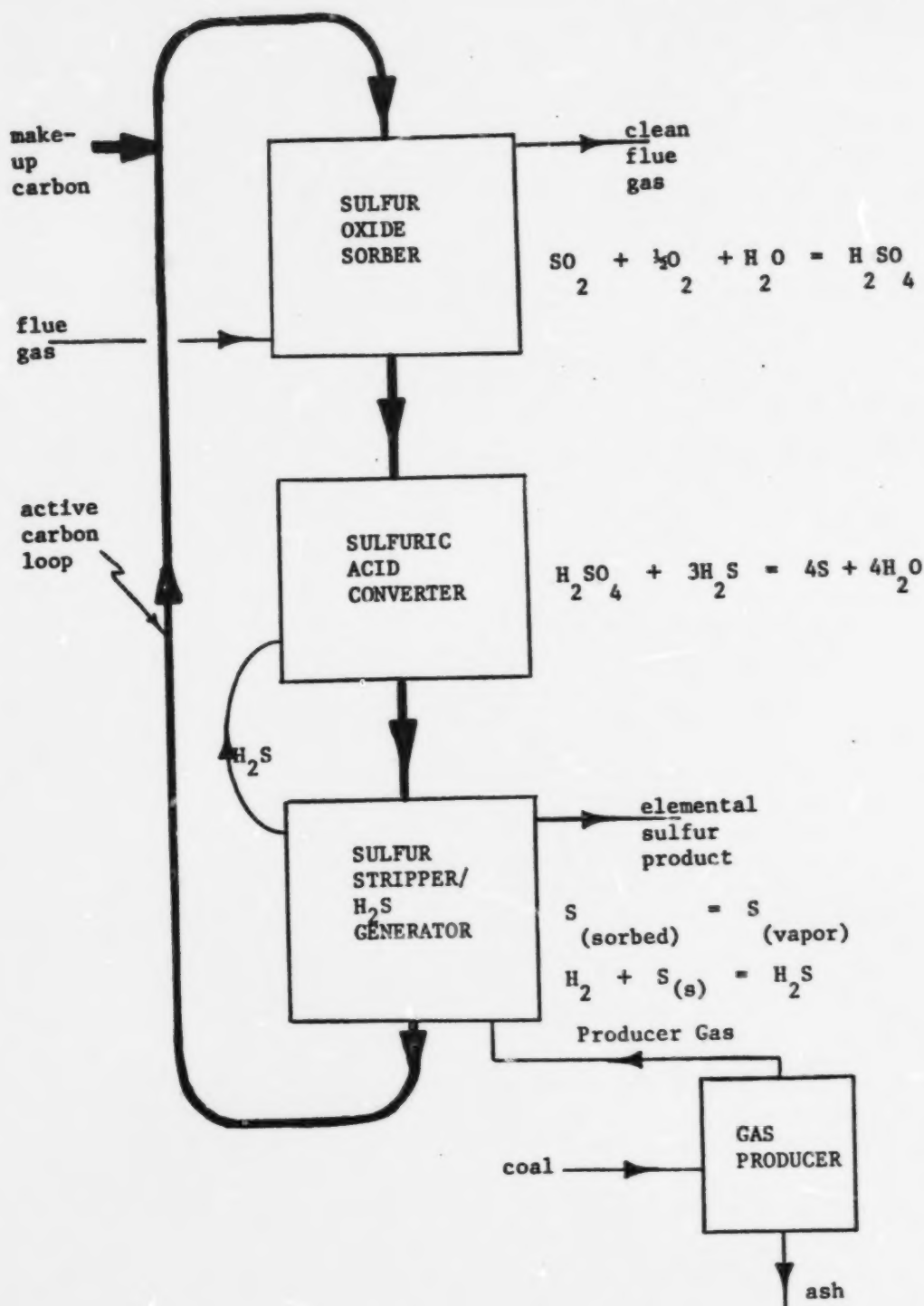
The sulfur recovery loop, in which carbon is regenerated, is distinct and separate from the gas scrubber. Carbon transfer is the only link between the scrubbing and regeneration sections.

Spent carbon is restored to its original effectiveness through two fluidized bed unit operations in which reactions (4) and (5) occur. Reaction (5) requires an external source of reducing gas, such as hydrogen.

Although hydrogen can be obtained by burning natural gas, LPG or petroleum distillates, the only fuel likely to be abundant in utility stations is coal. Therefore, a coal gasifier is featured as the source of reducing gas and process heat in this prototype installation.

A schematic flow diagram of the Catalytic/Westvaco process is presented on Page 6. This sketch illustrates the three major process units in which carbon is continuously saturated with SO_x and subsequently regenerated. The gas producer will be a present-generation coal gasification unit generating a low-Btu gas. A shift converter and clean-up train will form the interface between the gas producer and the main process.

CATALYTIC/WESTVACO FGD PROCESS SCHEMATIC



TECHNICAL APPROACH - PROTOTYPE UNIT

Project Scope

The technical feasibility of the Catalytic/Westvaco process has already been established in integral pilot plant tests. In order to obtain fundamental information for a detailed process scale-up and economic optimization, a demonstration program is proposed featuring the erection and testing of a 30-megawatt prototype (60,000 CFM measured at 60°F and 1 atmosphere). The scope of the proposed program is to assess process performance and to obtain engineering data in the following key areas:

1. Interface analysis
 - a) turndown, surges, upsets and outage in boiler
 - b) reliability and availability
 - c) fuel feed variations
 - d) safety
2. Control of process chemistry
 - a) response to upsets and variations (controllability)
 - b) long term stability
3. Performance of activated carbon
 - a) mechanical
 - b) chemical
 - c) poisoning and contamination
4. Performance of large scale fluid bed vessels
 - a) solids distribution
 - b) gas distribution
 - c) thermal gradients
 - d) ease of operation
 - e) materials of construction

In attaining these objectives the scope of this program includes:

1. Definition of boiler operating characteristics
2. Preparation of detailed prototype testing schedule
3. Preparation of prototype design specifications
4. Detailed engineering design and bid evaluation
5. Construction
6. Start-up
7. Operation
8. Data evaluation and process technical and economic assessment

The prototype plant will contain the following major processing capabilities:

1. SO_x removal from a fossil fuel boiler flue gas
2. Sulfur production from recovered SO_x
3. Thermal stripping of sulfur product and in-situ production of hydrogen sulfide
4. Condensation and recovery of the elemental sulfur product
5. Production of chemical reducing gas (hydrogen) by gasification of coal and shift conversion of carbon monoxide

As an adjunct to the prototype program, the scope of work will also include, as necessary, additional testing in the original pilot (and other) equipment to refine the prototype design with a view toward optimization.

General Design Basis

The basis for the design and cost of the proposed demonstration facility is outlined below. It is considered to be indicative of a "typical" coal-fired utility installation and, of course, must be re-evaluated for any specific application. This basis in no way suggests a limitation on the range of effectiveness of the Catalytic/Westvaco Process, but merely provides meaningful criteria for the development of technical and economic details.

1. Host Boiler Slipstream Characteristics:

- | | |
|--------------------|--------------------------------|
| a. Capacity: | 30 MW equivalent (60,000 SCFM) |
| b. Type of Fuel: | Coal (Bituminous) |
| c. Sulfur Content: | 3.5% |

2. Process Conditions

a. SO_2 Sorber

- | | |
|------------------------------|----------------------------------|
| 1) Contact Mode: | Gas/Solid Fluid Bed -- Stagewise |
| 2) Carbon Feed Rate: | 11,025 lb/hr. |
| 3) SO_x Inlet Rate: | 1,664 lb/hr. (about 2,800 ppm) |
| 4) SO_2 Removal: | 95% (min.) from inlet stack gas |
| SO_3 Removal: | 100% |
| 5) Temperature: | 150-300°F |

b. Sulfur Production

- | | |
|---------------------------|----------------------------|
| 1) Contact Mode: | Fluidized Bed -- Stagewise |
| 2) Carbon Feed Rate: | 11,025 lb/hr. (mean) |
| 3) Sulfur Formation Rate: | 2,337 lb/hr. |
| 4) Temperature: | 250-325°F |

c. Sulfur Stripping/H₂S Formation

- | | |
|---------------------------|--|
| 1) Contact Mode: | Fluidized Bed -- Stagewise |
| 2) Carbon Feed Rate: | 11,025 lb/hr. (mean) |
| 3) Chemical Design Rates: | Sulfur Stripping 700 lb/hr.
H ₂ S Formation 330 SCFM |
| 4) Temperature: | 750-1000°F |

d. Sulfur Recovery

- | | |
|-----------------|--------------------------------|
| 1) Type: | Condenser, Shell & Tube |
| 2) Duty: | 700 lb/hr. sulfur recovery |
| 3) Efficiency: | 99.5% recovery of Inlet Sulfur |
| 4) Temperature: | 250-300°F |

e. Gasifier

- | | |
|-----------------|------------------------------------|
| 1) Type: | Coal Feed with Steam/Air Blast |
| 2) Feed: | Bituminous Coal 3,000 lb/hr. (max) |
| 3) Product Gas: | 60 SCF Gas per lb. coal |

3. Active Carbon Characteristics

- | | |
|----------------------------|---|
| 1) Size: | 12x40 mesh nominal; 1.5 mm mean particle size |
| 2) Density: | 40 lb/cubic foot |
| 3) SO ₂ Number: | 75 (minimum) |
| 4) Attrition Number: | 30 (maximum) |

4. Instrumentation

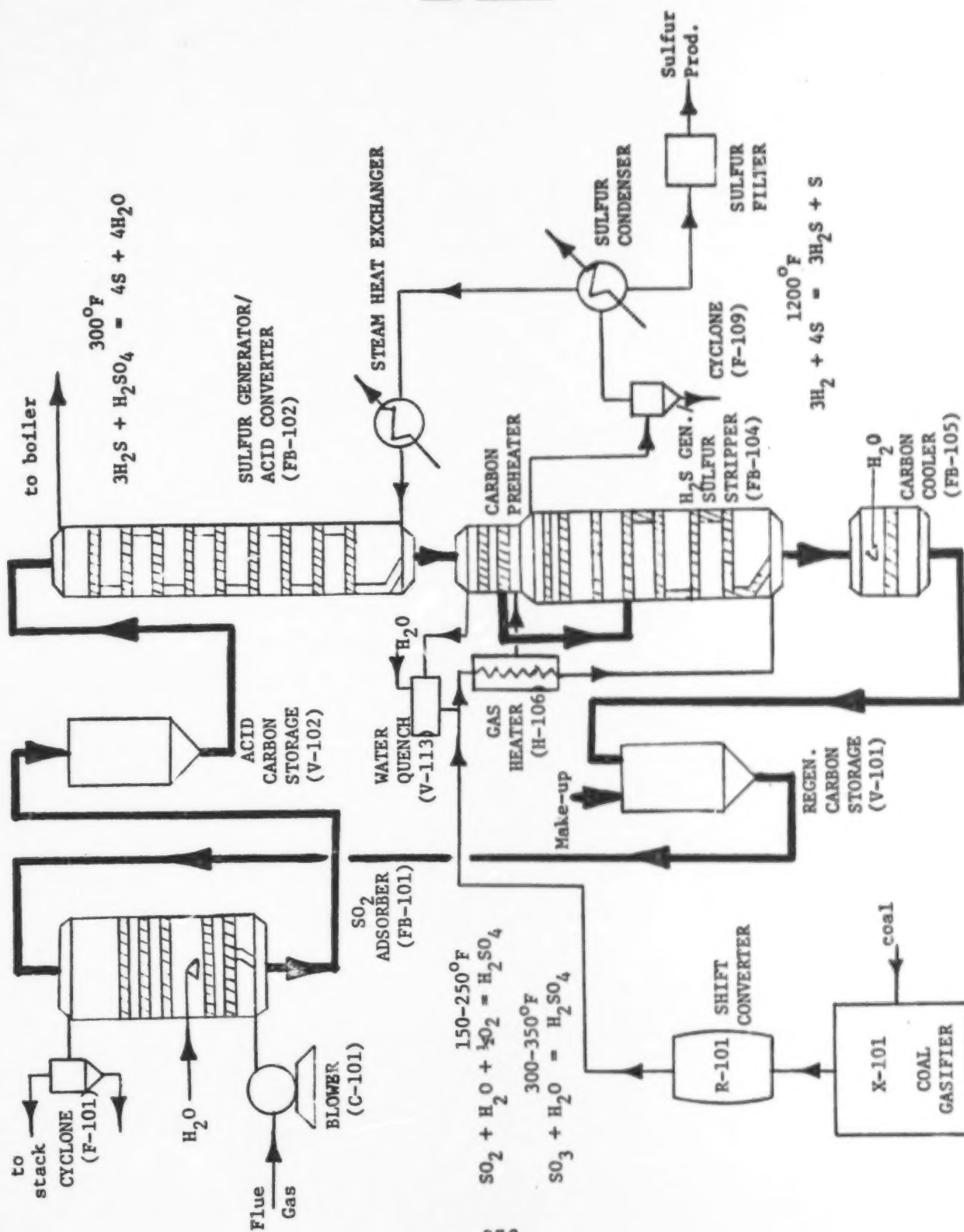
Adequate instrumentation is included to control and to monitor temperature, pressure, gas and carbon flow. Additional instrumentation is also included in the design to assess alternative methods of process control under the varying modes of utility boiler operation.

Detailed Process Description

The Catalytic/Westvaco prototype unit is described in this narrative and illustrated in the process flow diagram on Page 10. This diagram has been simplified for the benefit of the casual reader. For those desiring more detailed information, Engineering Flowsheets A-201 through A-204 are included in the Appendix, accompanied by a tabular material balance. Stream numbers and equipment designations employed throughout this paper are keyed to the engineering flowsheets for easy reference. (Some secondary equipment described in the narrative is not shown in the simplified flow diagram).

Flue gas leaving an electrostatic precipitator at approximately 300°F passes through a forced draft blower (C-101) into SO₂ adsorber (FB-101). The adsorber is 23 feet in diameter and contains five stages of fluidized activated carbon. Sulfur trioxide is removed from the hot gases in the bottom stage of the adsorber. Water sprayed into the second stage fluid bed cools the gas to 175°F prior to completion of 95% SO₂ removal in this and in the remaining three stages. Conversion of sulfur oxides to sulfuric

CATALYTIC/WESTVACO EGD PROCESS FLOW DIAGRAM



acid, an exothermic process, reheats the flue gas to approximately 215°F. A cyclone dust collector (F-101) removes entrained carbon dust from the flue gas prior to its exit through the stack. Recycled activated carbon continuously passes through the adsorber by gravity at a rate of 11,025 lbs./hr. When discharged, it is loaded with 22.0 lbs. H₂SO₄ per 100 pounds of carbon. The H₂SO₄ is produced by chemisorption, oxidation and hydrolysis of the SO_x in the flue gas.

Carbon leaving the scrubber is diverted to acid carbon storage silo V-102, from which it is fed to the regeneration system at a steady rate.

Sulfuric acid-laden carbon from the silo is fed to sulfur generator acid converter (FB-102) by a bucket elevator (M-107) and a feeder (W-103). In sulfur generator (FB-102), a 5'-3" diameter, 10 stage fluid bed, the sorbed sulfuric acid is converted to elemental sulfur by reaction with hydrogen sulfide at 300°F. The activated carbon becomes progressively loaded with elemental sulfur as it flows by gravity through the sulfur generator and exits with a loading of 20 lbs. sulfur per hundred pounds carbon. The sulfuric acid not converted to sulfur in this reactor will be converted in the top section of the H₂S generator/sulfur stripper/preheater (FB-104).

The elemental sulfur product is thermally stripped, and some sulfur is immediately converted to H₂S in H₂S generator/sulfur stripper (FB-104), which is a two-section unit. The 6'-7" diameter bottom section contains a total of seven stages - - three for H₂S formation and four for sulfur stripping. The carbon is preheated in the top two stages using reducing gas from gas heater H-106 at 1300°F, containing about 17% H₂. The carbon flows from the preheater section at 750°F, and bypasses the three H₂S formation stages to the four sulfur removal stages (at 1040°F). Any sulfuric acid remaining in the carbon after leaving the sulfur generator will react with the reducing gas to form sulfur and water. The off-gas from the carbon preheater passes to a quench tank (V-113) and is cycled at 200°F by a compressor (C-111) to the gas heater (H-106) for reheating. Additional 1300°F reducing gas from the gas heater (H-106) goes directly to the bottom of the H₂S generator/sulfur stripper where it contacts the carbon countercurrently to thermally strip the sulfur. The hydrogen and sulfur are subsequently converted to H₂S (necessary for sulfuric acid reduction in the sulfur generator). The gas leaves the H₂S generator/sulfur stripper at 1040°F and passes through cyclone (F-109) to a shell and tube sulfur condenser to recover the elemental sulfur. The liquid sulfur at 260-280°F is filtered of dust before storage. The cooled gas at 260°F is effectively free of sulfur. The regeneration gas is supplied by a coal gasifier (X-101) capable of gasifying anthracite, coke, charcoal, or bituminous coal. The gas from X-101 passes through a shift converter (R-101) before being used in the carbon preheater-H₂S generator/sulfur stripper.

Regenerated carbon from the H₂S generator at 1040°F is cooled to 300°F in carbon cooler (FB-105). Cooling is by evaporation of water sprayed over the single bed of fluidized carbon in the 6'-0" diameter unit. Inert gas, used as the fluidizing gas, passes through a cyclone (F-104), to a water condenser (E-103). The gas is recycled to the carbon cooler and condensed water is collected in a tank (V-104) for recycle.

The regenerated and cooled carbon is then returned to storage silo (V-101) for supply to the adsorber. Make-up carbon is added to this silo intermittently as needed.

Technical Alternatives

The foregoing design is sufficiently versatile to permit certain modifications in the interest of expanding the demonstration program or, conversely, reducing its overall cost. Several potential alternatives are described below:

Gasifier - The prototype plant contains a coal fired gas producer as a source of reducing gas (hydrogen). This route was chosen since most coal-fired utilities would prefer to use coal in this service rather than fuel oil, natural gas or liquified petroleum gas. Considerable savings in cost can be achieved by using an oil-fired gasifier in the demonstration effort. For a prototype plant in certain locations, fuel oil gasifiers may be an acceptable alternative.

Gas Cooling and Tar Removal - A spray water quench system was designed for the prototype plant in order to prevent plugging of tubular type coolers. By this means the cooling water can be utilized directly as part of the steam needed for shift conversion.

Shift Converter - A by-pass has been shown around the shift converter to allow for bypassing all or part of the producer gas. It is believed that activated carbon may "catalyze" the conversion of CO and H₂O in the production of H₂. It may be possible to eliminate the shift converter in a commercial plant. This possibility will be checked during the test run of the prototype plant.

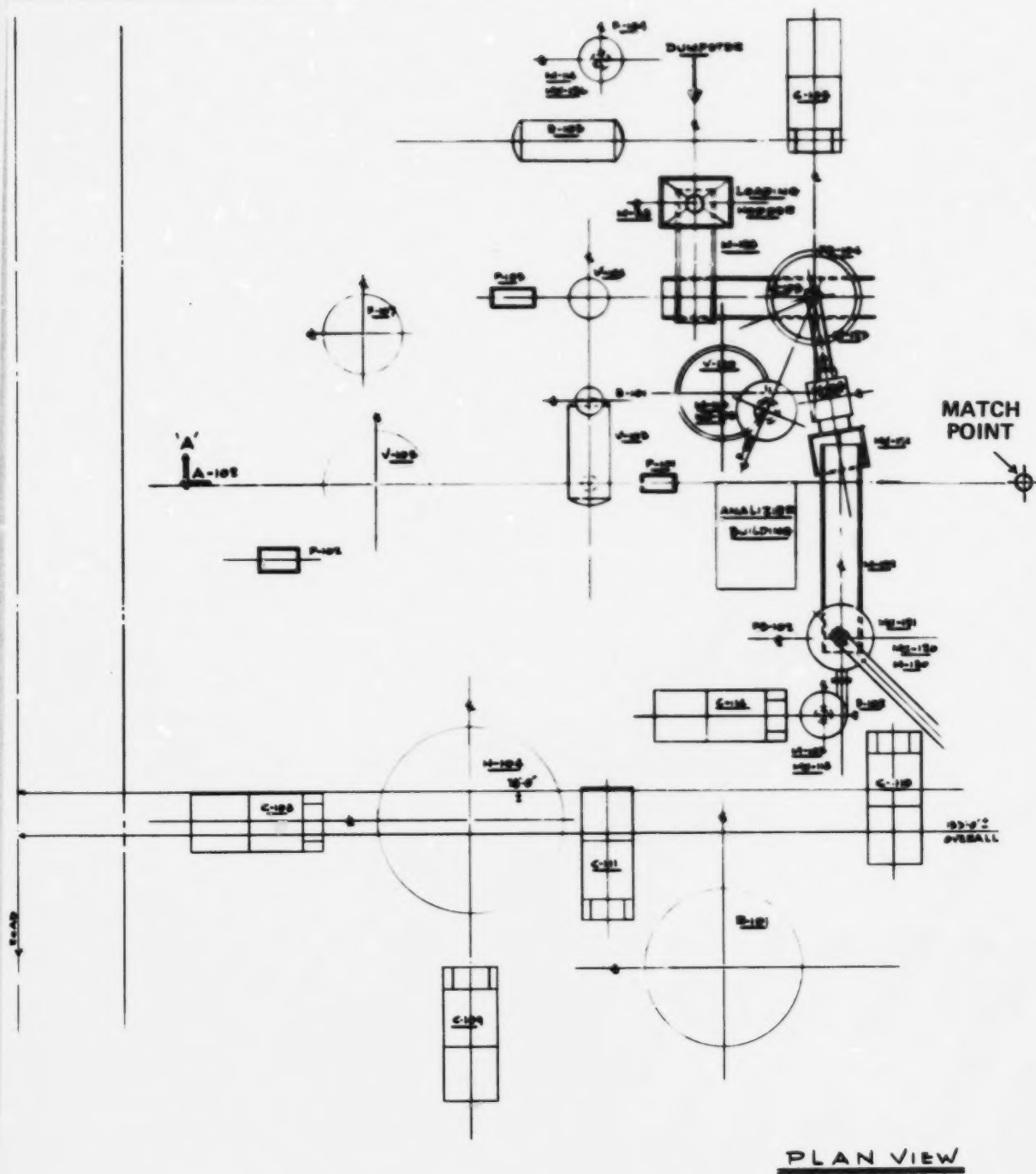
Flue Gas Inlet - Provision has been made in the design to bypass the electrostatic precipitator and enter the scrubber directly with flue gas. The design also allows for ducting scrubbed gas through the precipitator as the last step before entering the stack. (It may not be possible to conduct this test at some demonstration sites due to space limitations.) The purpose of this multiple path duct system is to test the long-range effects of flyash on the carbon system and to find the most efficient means of eliminating traces of carbon dust from the stack.

Equipment Arrangement

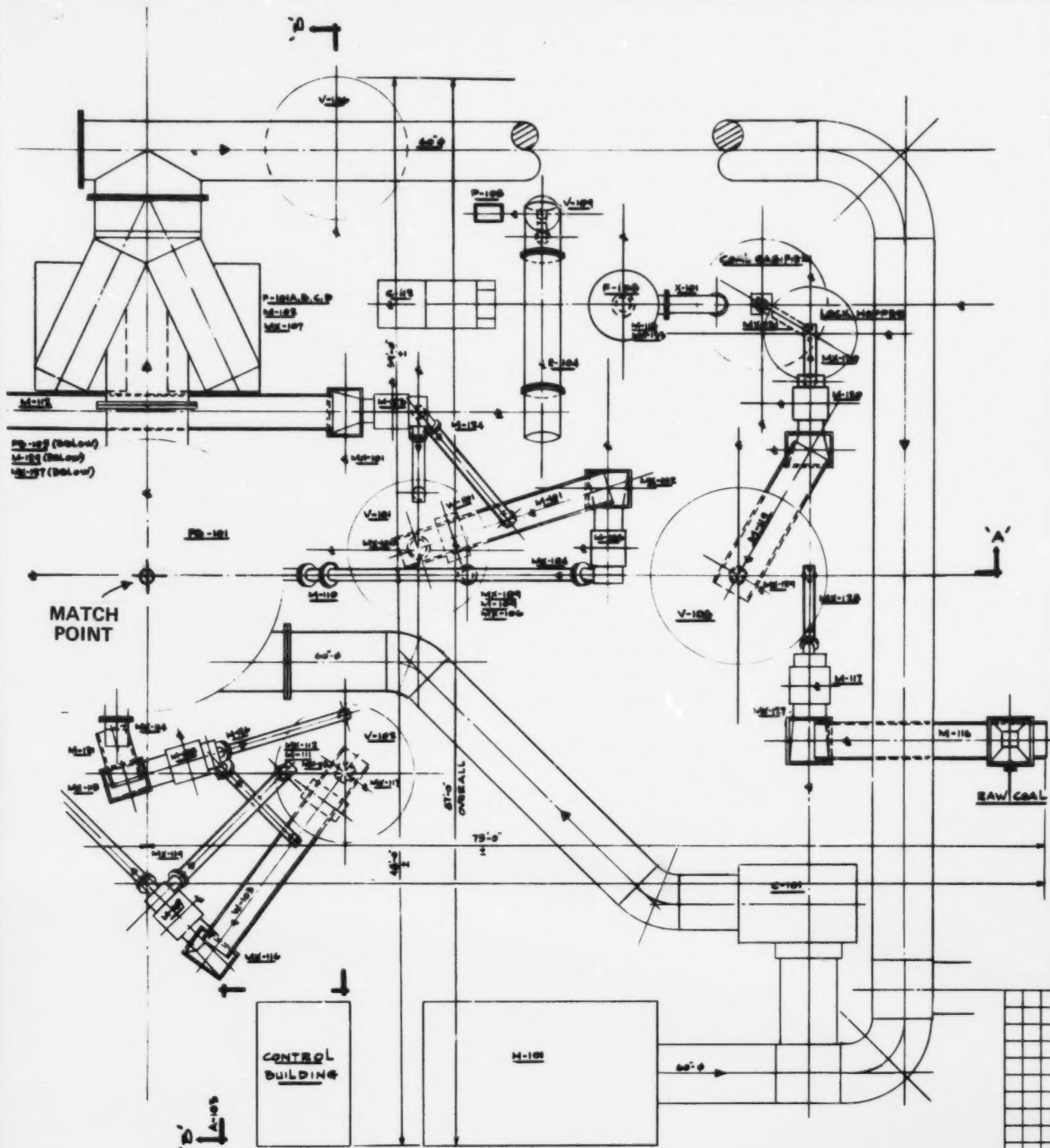
A clear area of approximately 100 x 130 feet will provide ample operating space for the proposed Catalytic/Westvaco prototype plant. Ideally, the site selected should be near the power boiler gas exit duct to facilitate tie-in. It should be unobstructed overhead since some of the carbon elevators will reach a height of approximately 100 feet.

It was assumed in developing this program that electric power, steam, domestic water, boiler feed water and instrument air will be supplied by the host utility at the battery limits of the demonstration plant.

A potential Equipment Arrangement is given in Catalytic Drawing A-101, which follows this page.



PLAN VIEW



THIS DRAWING IS THE PROPERTY OF CATALYTIC, INC. THE INFORMATION CONTAINED HEREIN IS NOT TO BE COPIED OR REPRODUCED IN ANY MANNER WITHOUT THE WRITTEN PERMISSION OF THE COMPANY.		WESTVACO ACTIVE CARBON 530 PROCESS PROVIDED BY CATALYTIC, INC. ENGINEERING DEPARTMENT, PHILADELPHIA, PENNSYLVANIA	
SCALE: 1/8" = 1'-0" DRAWN BY: W.P. HODGSON CHECKED BY: J. H. HODGSON CATALYTIC, INC. PHILADELPHIA, PA.		DATE: 12-10-50 SHEET NO.: A-101 TOTAL SHEETS: 1	
REVISIONS:		EQUIPMENT ARRANGEMENT	

DEMONSTRATION PROGRAM

General Objectives

The overall intent of the proposed program is to demonstrate the Catalytic/Westvaco Process on a coal-fired boiler slipstream. Prior to actual engineering of the test unit, a comprehensive operating program and overall process specifications for the unit will be developed. These will be used by Catalytic as a basis for detailed design of the system. Prior to start-up, Catalytic will train technicians and operators to perform "hands-on" duties during the start-up, test and demonstration periods. Data reduction, evaluation and process assessment will be performed by Catalytic with appropriate assistance by Westvaco.

As an adjunct to the prototype design, tests will be made to evaluate proposed control modes, operating ranges and design features of the prototype unit. Input from these evaluations will be used to modify and to optimize the process design.

Program Elements and Schedule

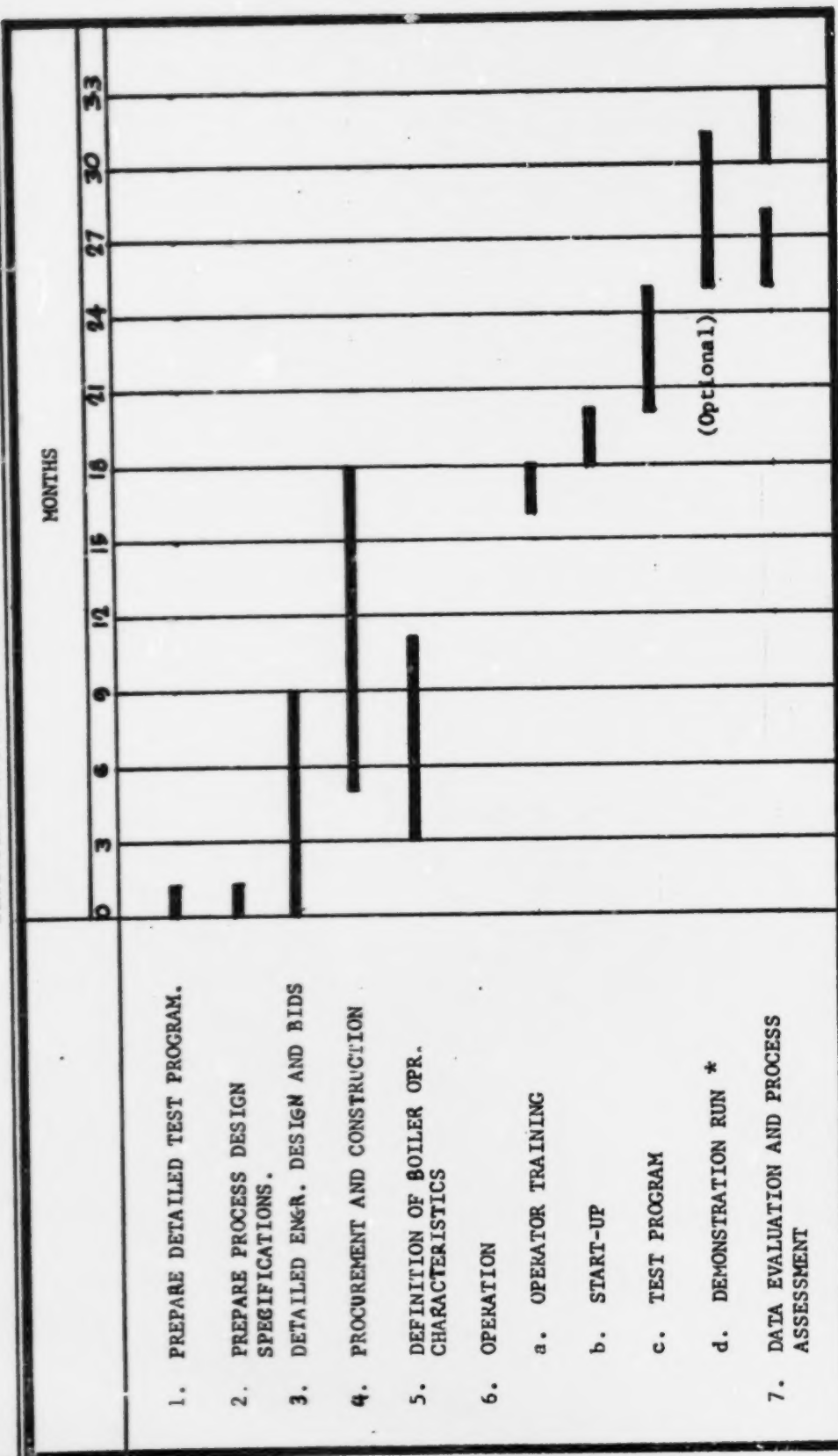
The operating schedule for the prototype plant calls for a two-month period of start-up, a six-month test program and an optional six-month demonstration run. The scheduled activities are presented in chart form on Page 16.

The start-up period will be used to place all units individually and jointly into operation, checking their operability over specified temperature, flow and pressure ranges, and to make any required adjustments or modifications. At the conclusion of the start-up period, the plant will be ready for an extended continuous test run accepting flue gas and circulating carbon through the adsorption and regeneration equipment on an integrated basis.

The initial operating period will be devoted primarily to establishing the operating characteristics of the process. A material and energy balance will be obtained and compared with calculated values. The SO₂ removal capability per carbon cycle, as a function of the number of cycles, will be determined. The process control characteristics, particularly stability and turndown capability, will be verified. These data will be analyzed as they are obtained. At the conclusion of the initial operating period, the data will be reviewed and any changes needed in the program for demonstration operation will be made.

The schedule chart presented on Page 16 contains a six month demonstration run (Item 6-d) which has not been included in the operating budget presented on Pages 18 - 20. It is expected that the budgeted test program (Item 6-c) will provide the fundamental data required to assess the viability of the process. An additional run may be desirable to establish industry-wide confidence in the technology.

**WESTVACO SO₂ REMOVAL
PROTOTYPE PROGRAM SCHEDULE**



* Demonstration Run has not been considered in the economic assessment of the costs to implement this program.

DEMONSTRATION PROJECT COSTS

Estimating Bases

The estimate presented in this section reflects all the costs associated with designing, constructing and operating the subject prototype/demonstration module of the Catalytic/Westvaco Flue Gas Desulfurization Process. The estimate as presented is for an undetermined but "typical" site. The equipment costs are based specifically upon the following attached drawings: A-101 (Equipment Arrangement) and A-202 through A-204 (Engineering Flow Diagrams).

The project completion schedule to which the estimate is tied is predicated upon starting engineering on 1 May 1976, beginning construction on 1 January 1977 and completing construction on 30 October 1977. The estimate is based on December, 1975 dollars. Appropriate escalation to carry through the construction period is included in the calculations.

The estimate is an order-of-magnitude type, based upon major equipment costs. Information for the major equipment items was obtained by several methods. In the case of the fluid bed towers (FB-101, 102, 104 and 105), two prospective vendors were each asked to quote on designs and fabrications. On items of mechanical equipment (pumps, compressors, blowers and miscellaneous conveyors), vendors with whom Catalytic has continuous contact submitted estimates based upon Catalytic equipment data sheets. Items such as heat exchangers and vessels were estimated in-house using recent quotations and experience. The gasifier package, X-101, is based upon the Wellman-Galusha Agitated design, 6.5 feet in diameter. Vendor pricing was obtained for approximately 90% of the major equipment costs.

Estimates for other materials (piping, instrumentation, electrical, etc.) were calculated by one of two methods. Whenever possible, engineering estimates were made based upon preliminary takeoffs. This method was used for piping, instrumentation, electrical, concrete, steel, insulation, painting, chemicals and catalyst, and ductwork. Where such a technique was not feasible, allowances based upon experience were made (as in the case of sewers, site development and fire protection). The buildings were priced on a per-square-foot basis.

As previously stated, the capital cost estimate is for an undetermined site. An hourly craft labor rate of \$10.00, including fringes, was used in calculating labor costs, and a payroll burden of 12% was assumed. Productivity was assumed to be comparable to Gulf Coast standards. When a specific site is selected, these factors plus items such as sales or use taxes must be re-evaluated.

Catalytic's Home Office Service includes detailed Engineering and follow-up support throughout construction. Costs for these tasks were prepared as follows: Each engineering Division Chief Engineer used his experience and judgment to estimate the manpower requirements necessary to fulfill his discipline's responsibilities efficiently and on schedule.

Installed Cost

The installed cost for a 30-megawatt demonstration module of the Catalytic/Westvaco FGD Process has been estimated at \$5.85 million. This cost reflects process design capability for continuous SO_x removal in excess of 95% when raw flue gas issues from a coal-fired boiler fitted with an electrostatic precipitator. The inlet SO_x concentration corresponds to a 3.5% sulfur coal.

A breakdown of the installed cost estimate is presented below. These figures take into account the nature of the proposed installation as a demonstration plant, containing considerable reserve capacity and fully adaptable for a rigorous experimental program. Therefore, it would be inaccurate to scale the numbers in order to estimate the costs of a commercial installation. Catalytic will provide, on request, realistic costs for large-scale commercial systems.

PRELIMINARY INSTALLED COST ESTIMATE

Material, subcontracts, shop labor	\$4,050,000
Total field charges and payroll burden	666,000
Total Home Office charges	600,000
Contingencies and escalation	336,000
Overhead and Fee	<u>198,000</u>
Installed Cost	\$5,850,000

Operating Costs

A summary of operating costs for the proposed demonstration program is presented below. Of the \$1.24 million project budget, 46% is allocated for utilities and chemicals, with 21% for operating labor. Maintenance is estimated at 4.5% of the installed cost (on an annual basis) and plant overhead is 20% of the sum of items (1), (2) and (3) below. The operating labor force includes 3½ operators per shift (average of 4 shifts per day), a Plant Superintendent, Lab Technician, Secretary/Clerk, Developmental Process Engineer and Demonstration Program Manager. A summary of utilities and chemicals requirements are given on Page 20.

Since the proposed program is primarily for testing and demonstration, the attached operating costs have been developed on a conservative basis, including significant reserves of utilities and chemicals and an expanded operating labor roll. Catalytic will supply, on request, operating data applicable to large-scale commercial installations.

SUMMARY OF OPERATING COSTS

Direct Costs

(1) Operating Labor, Payroll Burden and Training	\$ 262,000
(2) Maintenance - Material, Labor and Supplies	150,000
(3) Utilities and Chemicals (Not including initial charges)	566,000

Indirect Costs

(4) Plant Overhead (Approximate)	<u>195,600</u>
	\$1,173,700
Travel	20,000
Laboratory Analyses	20,000
Computer Usage	5,000
Miscellaneous	<u>20,400</u>
Total Operating Program*	<u>\$1,239,000</u>

* Includes: Operator Training (1 month)
Start-up (2 months)
Program (6 months)

Not Included: Demonstration Run (Optional) (6 months)

Utilities and Chemicals

Basis: 6 month program + 2 month start-up:

Total - 8 months at 80% utilization = 4675 hours

<u>Item</u>	<u>Rate of Usage</u>	<u>Rate of Cost</u>	<u>Total Usage</u>	<u>Total Cost</u>
Electricity	1800 KWh/Hr.	0.025/Kwh	8,415,000 KWh	\$210,400
Coal	1.5T/Hr.	\$25/T	7,000 T	175,000
Steam	2900#/hr.	\$3.00/M lb.	13,550,000 lb.	41,000
Demin. Water	38.4 GPM	\$3.00/M Gal.	10,800,000 Gal.	32,000
Instrument Air	100 cfm	0.05/M scf	28,000,000 scf	14,000
Cooling Water	340 GPM	0.10/M Gal.	95,300,000 Gal.	9,000
Activated Carbon	20#/hr.	\$0.50/lb.	93,500 lbs.	46,700
Catalyst				5,500
Carbon & Catalyst loss due to Cleaning, Maintenance and spills during startup and tests - 90,000 lbs.				45,000
Total Utilities and Chemicals Based on 4675 hours				\$ 566,000

Allocation: Start-up (2 mo.) = \$170,000

Program (6 mo.) = \$396,000

CONCLUSIONS AND RECOMMENDATIONS

Among various techniques for controlling sulfur oxides emission, post-combustion gas scrubbing is expected to predominate during the 1980's. Regenerable FGD processes producing useful effluents, such as sulfur, should be in greatest demand. The Catalytic/Westvaco system shows great promise of competing successfully both technically and economically in this market. Full-scale commercialization of the technology is premature at this time, however, since additional data for scale-up and optimization purposes is still needed.

Clearly, a prototype demonstration facility -- large enough to supply reliable information yet small enough to be "affordable" -- is the next logical step. This prototype plant should be equipped to provide meaningful test results for Catalytic while serving as a representative and believable demonstration for the Utilities and for Industry. To this end, Catalytic welcomes comments and suggestions relating to the process or to the proposed demonstration program. In the same light, we will provide any information at our disposal to facilitate the analysis or evaluation of the technology. Catalytic's history is one of service to the chemical process industry. The organization has built a firm reputation for "making things work". The proposed demonstration project is viewed in this spirit.

ACKNOWLEDGEMENT

Much of the Westvaco's experimental data was developed under a contract partially funded by the U.S. Environmental Protection Agency, with Mr. Leon Stankus acting as project officer. EPA neither approves nor disapproves of the Catalytic/Westvaco FGD process.

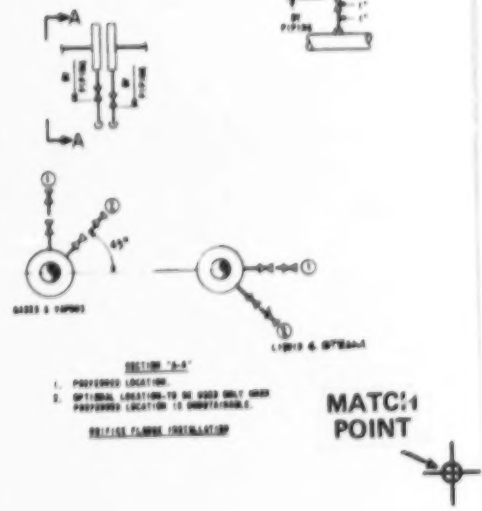
APPENDIX

The Appendix contains Catalytic's Engineering Flowsheets A-201 through A-204, which are followed by a tabular Material Balance. This information supplements the Detailed Process Description presented on Pages 9 through 12 of this report. Item designations and stream numbers presented on the Drawings are keyed to the Material Balance and to the preceding narrative.

SYMBOL	DESCRIPTION	SYMBOL	DESCRIPTION	SYMBOL	DESCRIPTION	SYMBOL	DESCRIPTION
	GATE VALVE		STEAM TRAP (SEE DETAIL)		INSTRUMENT - BY DETAIL		LINE GLASS (NOT INSTANT-ON/INSTANT-OFF)
	GLOBE VALVE		LINE FILTER		INSTRUMENT - BY DETAIL		LINE GLASS (NOT INSTANT-ON/INSTANT-OFF)
	BALL VALVE		FLANGE ASSEMBLY		CONTROL VALVE		LINE GLASS (NOT INSTANT-ON/INSTANT-OFF)
	CHECK VALVE		OPTURE DISC		F.C. (FAIL OPEN) F.C. (FAIL CLOSED)		LINE GLASS (NOT INSTANT-ON/INSTANT-OFF)
	DIAPHRAGM VALVE		ROTOMETER (R)		GAGE PRESSURE REGULATOR (SELF CONTAINED)		PRESSURE - INSTRUMENT WITH SAMPLE CONNECTION
	PLUG VALVE		POSITIVE DISPLACEMENT FLOW METER		PRESSURE REDUCING REGULATOR (SELF CONTAINED)		PRESSURE - INSTRUMENT HANGING
	THREE-WAY VALVE		INSTRUMENT AIR SUPPLY		PRESSURE REDUCING REGULATOR (LINE ACTUATED)		PRESS. GAGE, INSTANT HANGING
	FOUR-WAY VALVE		VESSEL SUPPLY		CONTROL VALVE ASSEMBLY (P) VALVE POSITIONER		PRESSURE - INSTRUMENT WITH SAMPLE CONNECTION
	BUTTERFLY VALVE		FLEXIBLE HOSE		ISOLATED EQUIPMENT		PRESSURE - INSTRUMENT WITH SAMPLE CONNECTION
	SAMPLE CONNECTION		PRIMARY PROCESS LINES		ELECTRICALLY TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	RESIDUE VALVE		AUXILIARY & UTILITY LINES		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	MOBILE VALVE		PNEUMATIC INSTRUMENT LINE		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	PRESSURE SAFETY VALVE		ELECTRICAL LINE		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	CYLINDER OPERATED VALVE		CAPILLARY TUBING		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	TWO-WAY SOLENOID VALVE		HYDRAULIC LINE		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	THREE-WAY SOLENOID VALVE		ELECTROMAGNETIC OR SONIC SIGNAL		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	FOUR-WAY SOLENOID VALVE		PACKAGE UNIT (SUPPLIED BY VENDOR)		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	FLUSH BOTTOM VALVE		EXISTING OR FUTURE PIPING & EQUIPMENT		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	FLEXIBLE JOINT		ISOLATED LINE		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	FLANGED CONNECTION WITH BLIND FLANGE		STEAM TRACED & ISOLATED LINE		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	WELDED END CAP FITTING (SEE S. & S. W. PER PIPING SPEC.)		ELECTRICALLY TRACED & ISOLATED LINE		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	NOZZLE CONNECTION		INSTRUMENT - BOARD MOUNTED (REMOTE PANEL)		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	LINE STRAINER WITH VALVE		INSTRUMENT - BOARD MOUNTED (LOCAL PANEL)		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	ORIFICE FLANGE ASSEMBLY		INSTRUMENT (BACK OF PANEL)		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	FIBROUS LINING		INSTRUMENT (LOCAL MOUNTED)		STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING
	SIGHT GLASS				STEAM TRACED & ISOLATED EQUIPMENT		PRESS. GAGE, INSTANT HANGING

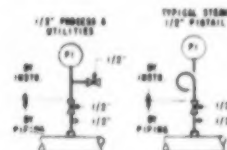
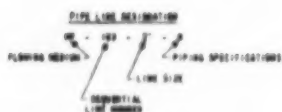
FIRST LETTER		SUCCEEDING LETTERS (2)	
	HEADSTOCK OR SUFFIX OR VARIABLE (4)	HEADSTOCK OR PREFIX FUNCTION (3)	SUFFIX FUNCTION (3)
A	Analysis (8)	Along	User's Choice (1)
B	Bar	Bar or Chart (1)	User's Choice (1)
C	Collection		
D	Chemical		
E	Electricity		
F	Electricity (Special) or Specific	D. A. Control (4)	
G	General (8)		
H	Height (8)		
I	Volume (8)	Primary Element	
J	Price (8)		
K	Group	Class (8)	
L	Low (8)		
M	Material (8)		
N	Normal		
O	Control (8)		
P	Power	Indicate (18)	
Q	Power or Temperature		
R	Low	Size (7)	
S	Station or Location		
T	Temperature		
U	Unit	Light (Pilot) (11)	
V	User's Choice (1)		
W	Water	User's Choice (8)	
X	Pressure or Temperature	User's Choice (8)	
Y	Pressure or Temperature	Temperature or Pressure (8)	
Z	Pressure or Temperature	Speed or Price	
AA	Pressure or Temperature		
AB	Pressure or Temperature	Switch (18)	
AC	Pressure or Temperature		
AD	Pressure or Temperature	Temperature	
AE	Pressure or Temperature	Measurement (12)	
AF	Pressure or Temperature	Value, Storage, or Location (12)	
AG	Pressure or Temperature		
AH	Pressure or Temperature	Wall	
AI	Pressure or Temperature	Uncontrolled	
AJ	Pressure or Temperature		
AK	Pressure or Temperature		
AL	Pressure or Temperature		
AM	Pressure or Temperature		
AN	Pressure or Temperature		
AO	Pressure or Temperature		
AP	Pressure or Temperature		
AQ	Pressure or Temperature		
AR	Pressure or Temperature		
AS	Pressure or Temperature		
AT	Pressure or Temperature		
AU	Pressure or Temperature		
AV	Pressure or Temperature		
AW	Pressure or Temperature		
AX	Pressure or Temperature		
AY	Pressure or Temperature		
AZ	Pressure or Temperature		

- NOTES
HARRIS APPROPRIATE
IN OUTSIDE THE CIRCLE
P. F. W. G. A. T. O. H. O. O. H. E. R.
P. F. C.
N. G. R. I. F. I. C. E. P. O.
P. A. R. A. M. I. T. A. S. I. E. S. P. O. P. U. L. A. T. I. O. N.
S. O. C. I. E. T. Y. O. F. A. M. E. R. I. C. A.
T. A. X. I. O. N. S. Y. M. B. O. L. I. S. M. A. N. D.
T. I. S. I. O. N. S. 1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20.

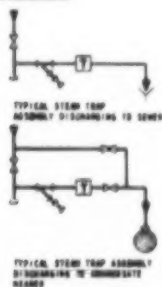


GENERAL NOTES

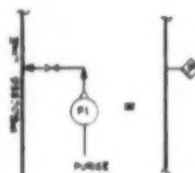
1. Piping sheet does not show all required vents & drains. These valves & lines will be included, where required on subsequent detailed piping drawings.
2. All equipment & vessel connections which are not specifically sized, shall be line size.
3. All control valves, instruments, vents & drains & block valves shall be traced & insulated liquid shall be traced & insulated.
4. Traced lines & vessels shall be traced & insulated up to and including first block valve only.
5. Where required, block valves shall be flanged to vessel nozzle.
6. All chemical drains shall discharge to chemical sewers. All water, oil condensate lines may discharge to ground.
7. U.S. Designated Utility Station.
8. S.S. Designated Safety Station.
9. E.W. Designated Eye Wash.
10. Unless otherwise noted, contractor shall furnish all valves and instruments shown. Valves and instruments marked with the symbol "T" will be furnished as part of a vendor package.
11. Block valves shall be line size. Or-pass valves shall be same size as control valve. Or-pass valves 3" and smaller shall be block valves unless otherwise designated.



TYPICAL PI INSTALLATION



TYPICAL STEAM TRAP ASSEMBLY DISCHARGING TO SEWER

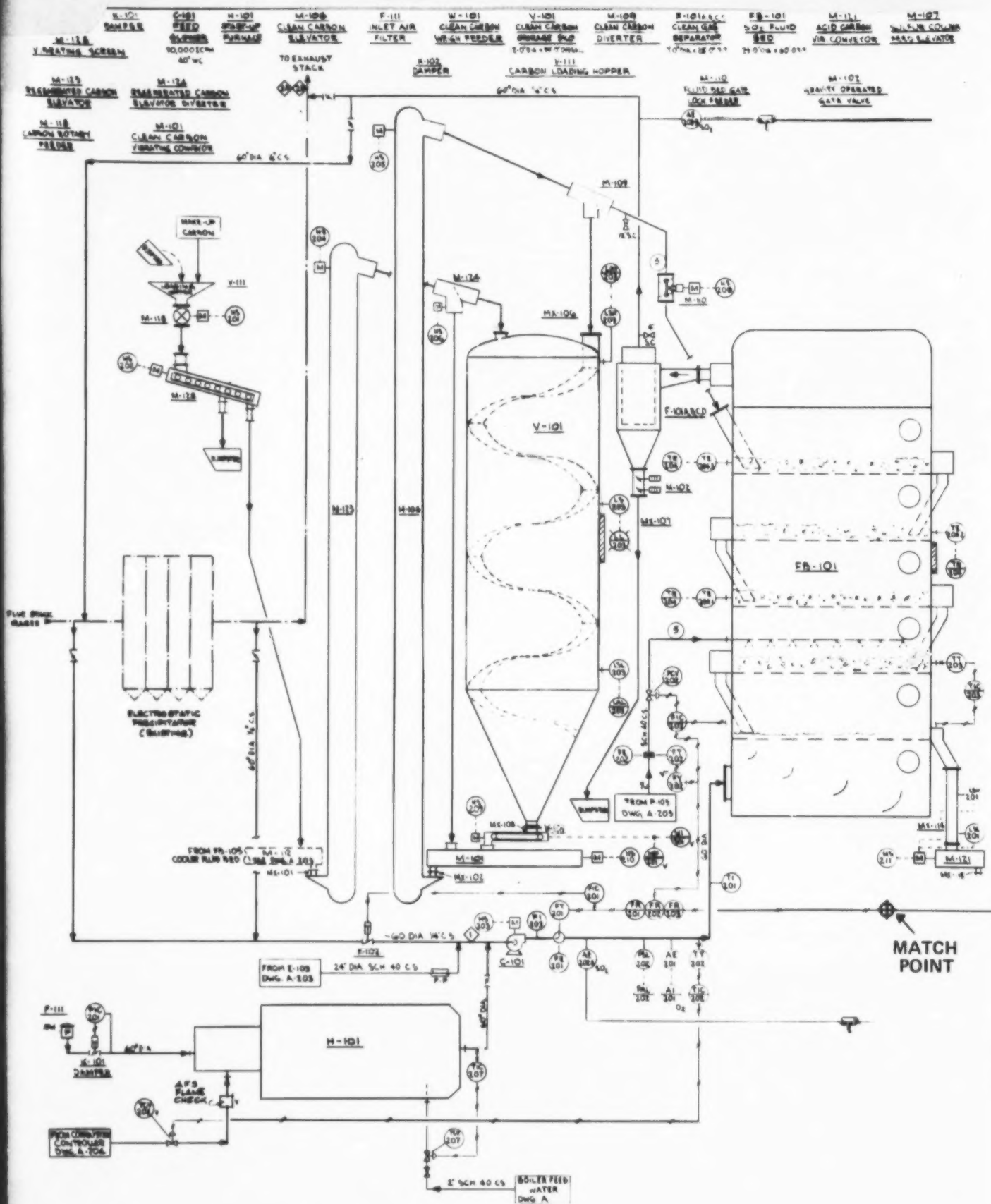


TYPICAL PURGE



MATCH POINT

THIS DRAWING IS THE PROPERTY OF CATALYTIC, INC. THE INFORMATION CONTAINED HEREIN MAY NOT BE USED OR REPRODUCED IN ANY MANNER WITHOUT THE WRITTEN PERMISSION OF THE COMPANY.									
DESIGNED BY: J. E. HALL DATE: 7-6-78									
CHECKED BY: J. E. HALL DATE: 7-6-78									
APPROVED BY: J. E. HALL DATE: 7-6-78									
PROJECT NO. 38720 SHEET A-201									



M-116
COAL VENT
SERIAL

M-117
CON. RICHET
ELEVATOR

V-108
COAL SILO
15'-0" X 50'-0" HT.

M-118
GAS FIVE COAL
LOCATING UNIT

M-120
GAS FIVE COAL
LOCATING UNIT

A-101
COAL GASIFIER
PACKAGE

F-108
CYCLONE
COLLECTOR

C-112
PRODUCER GAS COMPRESSOR
2200 SCFM
@ 11 PSIG
M.P.

V-112
RAW COAL LOADING
HOPPER

F-112
SILO VENT
FILTER

M-117
COAL SILO
LIVE FROM BOTTOM

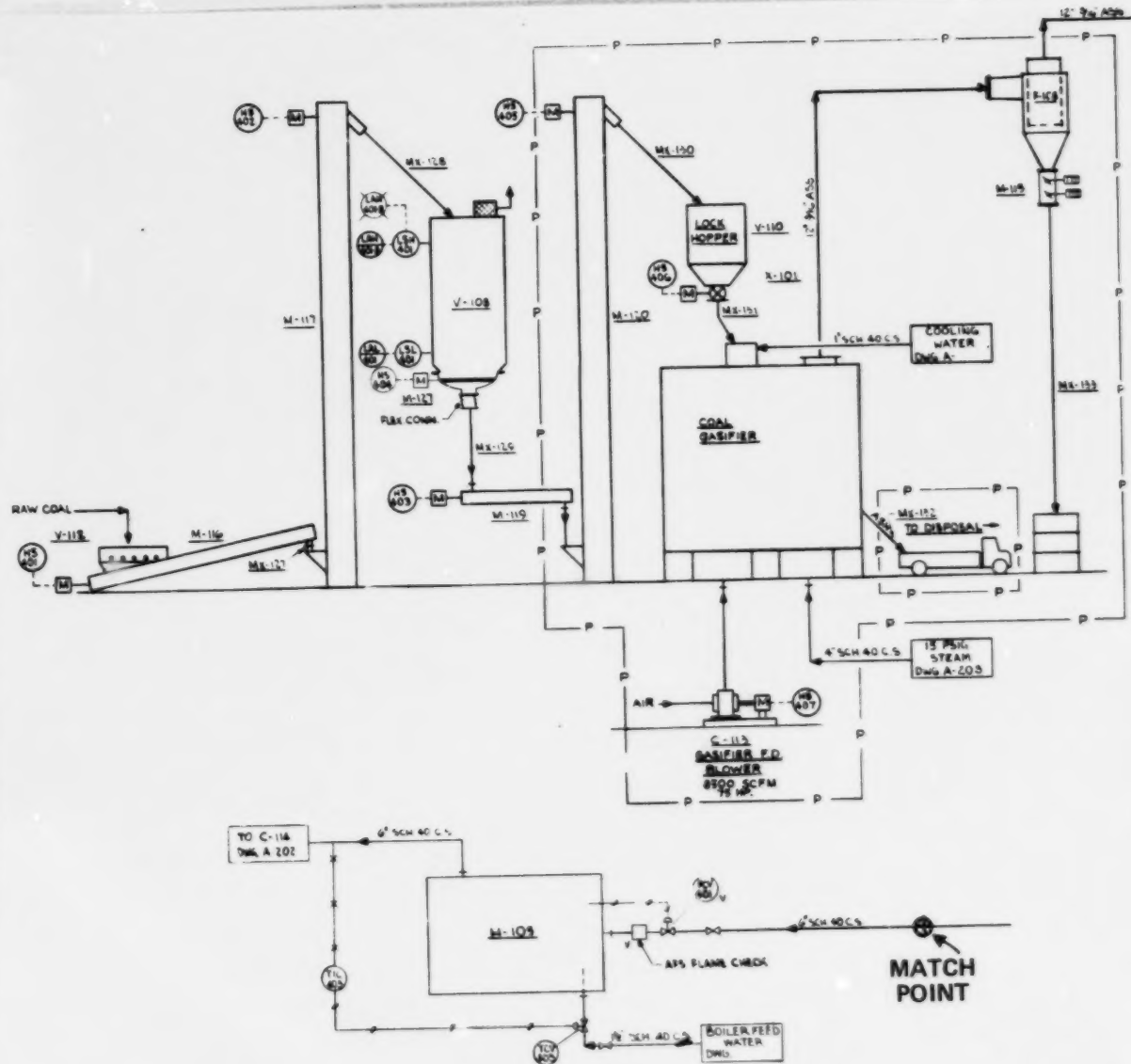
M-104
INERT GAS
GENERATOR

V-110
LOCK HOPPER

M-121
GASIFIER FEED
ROTARY VALVE

M-118
GASIFIER OPERATOR
GATE VALVE

A-102
COMP. SYSTEM CONTROLLER
PACKAGE



~~E-100
COMPRESSION RATIO
COOLER
2200 BTU/HR~~



THIS MESSAGE IS THE PROPERTY OF CATALYTIC INC. THE INFORMATION CONTAINED HEREIN IS NOT TO BE DISCLOSED TO ANY OTHER PARTY WITHOUT THE WRITTEN PERMISSION OF THE OWNER.			THE WESTVACO	
MADE IN CHINA			PROPERTY OF CATALYTIC INC. INDUSTRIAL DEPARTMENT, 700 ARDEN PARKWAY, N.W.	
SERIAL NO. 55920			ENGR. FLOW DIAGRAM PRODUCER GAS	

○ ALL SOLIDS STREAMS - #/Hr.

◇ ALL GAS STREAMS IN LB. MOLES/HR.

COMPONENT	1	2A	2B	3	4	5	6	7
SO ₂	M.W. 64	26.0	1.3					3.71
H ₂	2.016							
H ₂ S	34						52.15	0.16
NH ₃	17							
CO ₂	44	1174.0	1174.0				62.87	62.87
CO	28	4.7	4.6				5.86	5.86
N ₂	28	6727.4	6727.4				118.11	118.11
O ₂	32	414.9	394.2		266			
CH ₄	16						5.46	5.46
H ₂ O	18	954.4	1392		428	8751	229.69	322.93
C ₂ H ₆	30						.99	.99
C	12		10.5	11,035.5	11,025			
Resid S	32		.5	441.5	441			
H ₂ SO ₄	98				2,426			
S	32							
TOTAL #/Hr. or lb/moles/hr.	9301.4	9693.5	11.0	11,477	14,586	8751	475.13	520.09
Temperature of	300°	216	216		300	160	260	300
Pressure PSIA	14.7	14.7					18.0	ATM
SCFM-GPM	59,994	62,523				17.5	3065	3355
ACFM	86,036	79,746					4164	4811
Density lbs/cu.ft.	0.061	0.058	40	40	40	61	0.049	0.043

SCFM = 70°F

○ ALL SOLIDS STREAMS - #/HR.

◇ ALL GAS STREAMS IN LB. MOLES/HR.

COMPONENT	(11B)	(9)	(10)	(11A)	(12)	(13)	(14)	(15)
SO ₂ M.W. 64								
H ₂ 2.016	35.36			70.01	24.22	105.37	81.15	33.62
H ₂ S 34	.47			.92	0.47	1.39	.92	.92
NH ₃ 17								
CO ₂ 44	31.99			62.08	31.99	94.07	62.08	14.55
CO 28	3.02			5.86	3.02	8.88	5.86	53.39
N ₂ 28	60.86			118.11	60.86	178.97	118.11	118.11
O ₂ 32		325	325					
CH ₄ 16	2.81			5.46	2.81	8.27	5.46	5.46
H ₂ O 18	112.36			210.91	130.75	323.27	152.87	86.06
C 12		11,025	11,025					
Resid S 32		441	441					
H ₂ SO ₄ 98		364						
S 32		2,218	2,337					
C ₂ H ₆ 30	0.51			0.99	0.51	1.50	0.99	0.99
TOTAL #/Hr. or Lb./moles/ hr.	247.38	14,437	14,128	474.34	254.63	721.72	427.44	313.10
Temperature °F	1217	300	751	1217	500	1217	823	534
Pressure PSIA	17.0			18.8	15.2	18.8	21.8	24.7
SCFM-GPM	1596			3059	1642	4655	2757	2020
ACFM	5050			9679	2974	14729	6674	3788
Density lbs/cu.ft.	0.0177	40	40	0.0177	0.0318	0.0177	0.0231	0.0366

○ ALL SOLIDS STREAMS - #/Hr.

◇ ALL GAS STREAMS IN LB. MOLES/HR.

COMPONENT	16	17	18	19	20	21 & 22	23	24
SO ₂ M.W. 64								
H ₂ 2.016							24.22	33.62
H ₂ S 34	52.15		0.31	0.31			0.47	0.92
NH ₃ 17								
CO ₂ 44	62.87		121.17	121.17			31.99	14.55
CO 28	5.86		11.29	11.29			3.02	53.39
N ₂ 28	118.11		227.64	227.64			60.86	118.11
O ₂ 32								
H ₂ 2								
CH ₄ 16	5.46		10.52	10.52			2.81	5.46
H ₂ O 18	229.69		177.39	275.22		1761	170.40	200.40
C ₂ H ₆ 30	0.99		1.91	1.91			0.51	0.99
C 12		11,015.5			11,015.5			
Resid S 32		441			441			
H ₂ SO ₄ 98								
S 240	2.91							
TOTAL #/Hr. or lb/moles/ 478.04		11,456.5	550.23	648.06	11,456.5	1761	294.28	427.44
hr.								
Temperature °F	1040	1040	160	300	300	160	200	600
Pressure PSIA	15.1		16.1	15.5			15.0	22.9
SCFM-GPM	3083		3549	4180		3.52	1898	2757
ACFM	8725		4152	5994			2364	5514
Density lbs/cu.ft.	0.0248	40	0.062	0.0479	40	61	0.045	0.028

THE SPRING-NOBEL HOECHST PROCESS FOR
SULFUR DIOXIDE RECOVERY FROM STACK GASES

W. H. Stark, H. A. Syme and J. C. H. Chu

Spring Chemicals Limited
Toronto, Canada

ABSTRACT

Nobel Hoechst Chimie of France and Spring Chemicals Limited of Canada have developed a regenerative process for flue gas desulfurization. The process uses an organic absorbent which is highly selective, possesses excellent stability and has a high capacity for absorption in the lower temperature ranges. It desorbs readily at higher temperatures producing a stream of SO_2 at a concentration in excess of 95% for liquefaction or conversion to sulfur or sulfuric acid.

A description of the process and flow diagram are presented. Capital and operating cost estimates for this process have been made based on the procedures used in EPA's January 1975 Detailed Cost Estimates for Advanced Effluent Desulfurization Processes. The resulting data are compared with the data given in the EPA report for alternative processes. Direct operating costs are also given for a representative range of SO_2 concentrations in the gas to process for other applications.

The Spring-Nobel Hoechst Process has application to flue gas concentrations of SO_2 ranging from power plant concentrations up to those levels which permit direct feed to sulfuric acid plants or conversion to elemental sulfur. It is being offered for recovery of SO_2 in stack gases from smelters, Claus plants and sulfuric acid plants among others and is ready for trials on power plant flue gas desulfurization.

THE SPRING-NOBEL HOECHST PROCESS FOR SULFUR DIOXIDE RECOVERY FROM STACK GASES

INTRODUCTION

Nobel Hoechst Chimie of France and Spring Chemicals Limited of Canada have developed a regenerative process for flue gas desulfurization. An aqueous solution of glyoxylic acid is used to absorb SO_2 . The absorbent is highly selective, possesses excellent stability and has a high capacity for absorption in the lower temperature ranges. It desorbs readily at higher temperatures producing a stream of SO_2 at a concentration in excess of 95% for liquefaction or conversion to sulfur or sulfuric acid.

The absorbent is produced by Nobel Hoechst Chimie of Puteaux, France who have developed the basic process data and obtained patents on the use of glyoxylic acid as an SO_2 absorbent. Spring Chemicals Limited have continued the process development and engineering including economic studies for a wide range of plant sizes and SO_2 concentrations in the gas to process. Spring, the exclusive world-wide licensee, is offering the process for flue gas desulfurization.

DESCRIPTION OF THE PROCESS

Figure 1 is a flow diagram of a typical application of the process. Gases enter the system through a direct contact cooler to bring the gases to the absorption temperature of approximately 35°C (95°F). Cooled gases enter the base of the tower where water is separated from the gases. For large applications such as coal burning power boilers where fly ash must be considered, the water flows to a sludge separation system and then to a pond or tower for cooling and returns to the direct contact cooler. For smaller applications and cleaner gases an indirect water cooled heat exchanger is a suitable alternative to the pond or tower. In either case the purge and water make up flows control the water balance of the direct contact cooling system.

The cooled gases pass upward through the required number of absorption stages of the tower where they contact a counter current flow of an aqueous solution of glyoxylic acid introduced to the top stage. The absorbent leaves the bottom

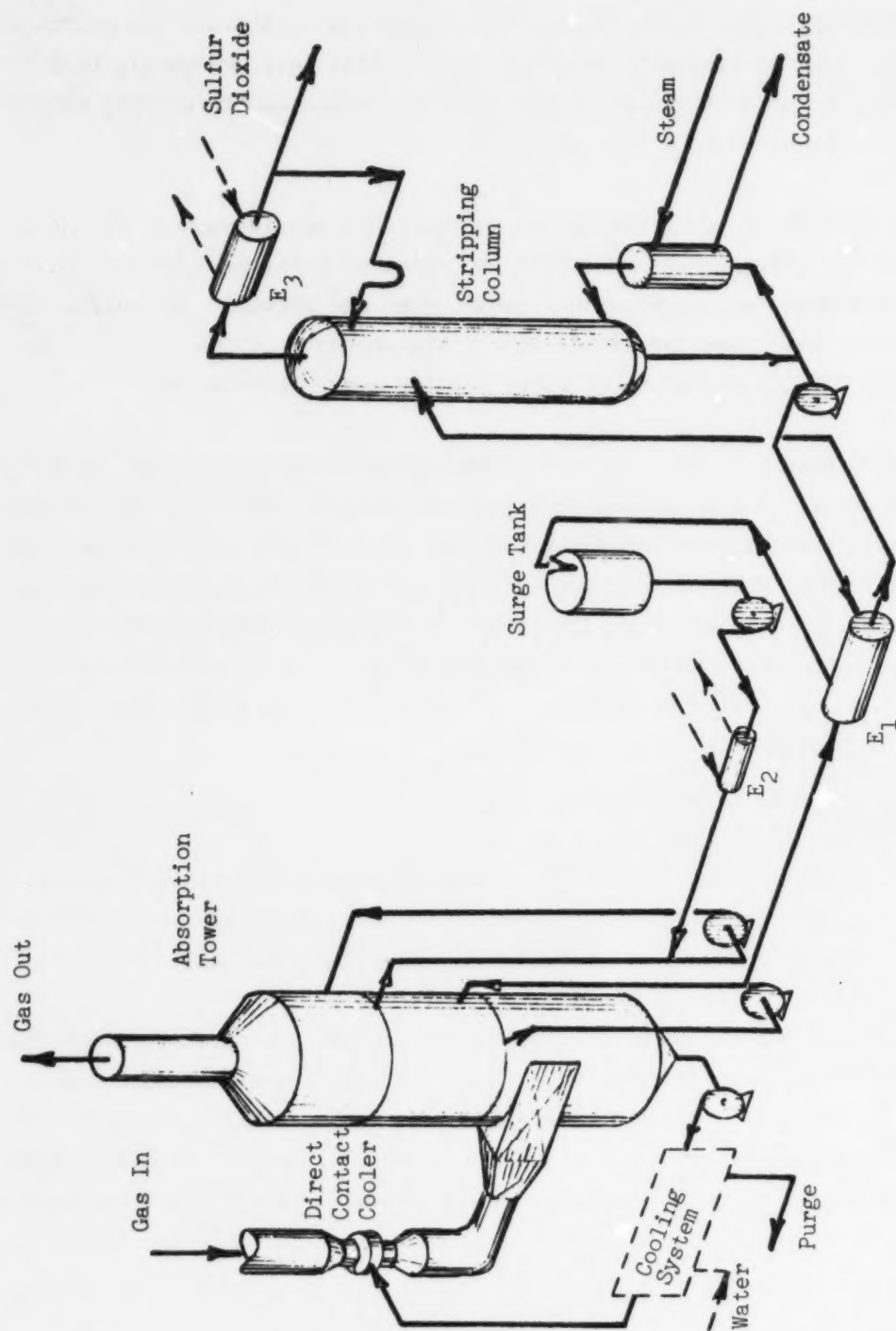


FIGURE 1

THE SPRING-NOBEL HOECHST PROCESS

absorption stage rich in SO_2 . Circulation pumps for each stage provide the proper ratio of liquid to gas flow. The absorption conditions are maintained within the range necessary to meet the SO_2 emission level which has been prescribed for the exit gases. These gases are reheated if required before discharge to atmosphere.

Absorbent rich in SO_2 from the bottom absorption stage is pumped to the upper section of the stripping column which is heated with indirect steam. Sulfur dioxide is removed as the absorbent passes down the column. The sulfur dioxide product exits the condenser at the top of the column at a concentration of about 95% SO_2 and 5% H_2O , dependent on plant cooling water temperatures.

The stripped absorbent from the column is pumped to the absorption tower top stage for reuse. A heat exchanger transfers sensible heat from the stripped absorbent to the absorbent entering the stripping column, reducing the heat input required at the column. A small heat exchanger on the absorbent feed line to the top stage provides final cooling which includes compensation for the heat of absorption to maintain the design operating temperature in the absorber. A tank incorporated into the system acts as a surge tank. A storage tank for absorbent make up is also included.

THE ABSORBENT

Three very important characteristics of this absorbent are the high degree of selectivity, the excellent stability under process conditions and the fact that there has been no evidence of sulfuric acid formation with this absorbent.

Glyoxylic acid is marketed world-wide for use in the pharmaceutical and chemical industries. It is an aldehydic acid. The formula of the monohydrate is $\text{HOOC}-\underset{\text{OH}}{\overset{\text{OH}}{\text{CH}}}$. The product has a number of uses in the chemical industry for manufacture of pharmaceuticals, cosmetics, plastics, rubber, textile, paper, dye and coatings, as well as others. It is marketed as a 50% aqueous solution.

PROCESS ECONOMICS

Cost estimates have been made for a number of different applications of this process. The design bases for these estimates have covered a wide range of feed gas rate and SO_2 concentrations. The capital and operating costs for the gas cooling and absorption system are a function of the gas to process, its temperature, flow rate and SO_2 content to and from the absorber. On the other hand, the desorption system costs are related to the quantity of SO_2 to be processed and to the SO_2 concentrations in the gas to and from the process. Accordingly a specific case has been selected for the preparation of comparative data on power plant flue gas desulfurization; the second case reflects the effect of SO_2 concentration on operating costs for other applications.

Power Plants

The U.S. Environmental Protection Agency has made and published an in-depth evaluation of Flue Gas Desulfurization Processes.¹ The published data are detailed and very well presented, permitting a good understanding of the design basis and costing methods used. Spring has selected the Base Case in the reference, a 500 mgw new boiler burning coal containing 3.5% sulfur as a basis for developing comparative capital and operating costs for the Spring-Nobel Hoechst Process. In developing these data, Spring has adhered to the design parameters and the scope of work as defined in the Base Case.

In the reference Base Case neoprene lined carbon steel was used for the contact cooler and absorber. For comparative costing Spring has followed the practice employing neoprene lined carbon steel shells and 316L stainless steel internals for the cooling and absorption equipment and all 316L stainless steel desorbers. At present the well established material of construction for the process equipment is 316L stainless steel. Its use for all material in contact with process streams would increase the investment for the Spring-Nobel Hoechst Process in this study by about \$2,000,000.

The capital estimates for cooling, absorption and desorption equipment prepared by Spring for this comparison are order of magnitude costs which fall within the range of +25 to -15% accuracy established in the reference Base Case study. Operating costs prepared by Spring are expected performance values.

For ease of comparison, these data and the reference EPA data have been summarized in two tables. The first table presents capital and operating costs for the complete facility through to an H_2SO_4 product as defined in the EPA reference. The second table provides a more direct comparison of the regenerative processes by excluding the costs downstream of SO_2 desorption; the costs of the Lime Slurry and Limestone Processes through to disposable sludge are shown again for information.

Table 1 summarizes the capital investment and operating costs for the Spring-Nobel Hoechst Process including the sulfuric acid plant at the EPA report costs and compares these combined costs to the costs for the Magnesium Slurry and Catalytic Oxidization Processes producing H_2SO_4 , the Sodium Solution Process which produces elemental sulfur and the Limestone and Lime Slurry Processes which yield a disposable sludge. The capital investment of \$26,470,000 for the Spring-Nobel Hoechst Process compares favourably to the other processes as do the operating costs of 2.283 mills per kwh compared to 2.20 to 2.31 for the disposable sludge processes and to 2.63 to 3.31 mills per kwh for the other regenerative processes.

Table 2 summarizes the capital investment and operating costs for the process through to the intermediate product SO_2 compared to the same point in the Magnesium Slurry Process and the Sodium Solution Process where SO_2 is produced as an intermediate process stream and to the Limestone and Lime Slurry Processes which produce a disposable sludge. The capital investment of \$20,060,000 for the Spring-Nobel Hoechst Process compares favourably with the other processes. The operating costs including fixed charges totalling \$6,199,000 per year, or 1.767 mills per kwh, are substantially lower than the operating charges for flue gas desulfurization for the other processes which range from \$7,703,000 to \$9,580,000 per year.

Other Stack Gas Desulfurization Applications

The process has application to stack gases from smelters, Claus Plants, sulfuric acid plants and other industrial operations. The engineering evaluation of a number of these applications provides data which illustrates the effect of SO_2 concentrations in the feed gas on the direct operating costs with this process.

TABLE 1

FLUE GAS DESULFURIZATION SYSTEMS FOR POWER BOILERS
THROUGH TO H_2SO_4 , SULFUR OR SLUDGE¹

PROCESS	UNIT OPERATING COSTS					CAPITAL DOLLARS INVESTED PER KW	END PRODUCT
	DOLLARS/TON COAL BURNED	DOLLARS/TON SULFUR REMOVED	DOLLARS/TON 100% H_2SO_4	CENTS/10 ⁶ BTU INPUT	MILLS/KWH		
Spring-Nobel Hoechst ²	6.09	221.78	72.43	25.38	2.283	52.94	H_2SO_4
Limestone Slurry	5.87	214.68	-	24.45	2.200	50.33	Sludge
Lime Slurry	6.17	225.81	-	25.72	2.310	44.84	Sludge
Magnesium Slurry	7.02	255.43	83.43	29.24	2.630	52.81	H_2SO_4
Sodium Solution	8.84	323.34	354.79	36.83	3.310	60.98	Sulfur
Catalytic Oxidation	6.76	247.32	80.75	28.17	2.540	85.47	H_2SO_4 (80%)

BASIS:

- U.S. Environmental Protection Agency data from Report EPA-600/2-75-006
500 mw new coal-fired power unit, 3.5% S in fuel; 90% removal;
15.8 tons/hr 100% H_2SO_4 .
No credit taken for recovered product.
Stack gas reheat to 79°C (175°F).
Midwest plant location represents project beginning mid 1972,
ending mid 1975, average capital cost basis mid 1974.
Minimum in process storage, only pumps spared.
Closed loop water utilization for gas cooling stage.
Investment for disposal of fly ash excluded.
Construction labour shortages with accompanying overtime pay incentive not included.
Operating costs are projected 1975 values.

- Spring estimates

TABLE 2

FLUE GAS DESULFURIZATION SYSTEMS FOR POWER BOILERS
THROUGH TO SO₂ OR SLUDGE¹

PROCESS	CAPITAL COSTS \$000'S	ANNUAL OPERATING COSTS \$000'S	DOLLARS/TON COAL BURNED	UNIT OPERATING COSTS-- DOLLARS/TON SULFUR REMOVED	CENTS/10 ⁶ BTU INPUT	MILLS/KWH	CAPITAL DOLLARS INVESTED/KW	END PRODUCT
Spring-Nobel Hoechst ²	20,060	6,199	4.71	171.71	19.61	1.767	40.12	SO ₂
Magnesium Slurry	18,974	7,528	5.73	208.77	23.90	2.149	37.95	SO ₂
Sodium Solution	23,590	9,580	7.30	267.00	30.41	2.733	47.18	SO ₂
Limestone Slurry	25,163	7,703	5.87	214.68	24.45	2.200	50.23	Sludge
Lime Slurry	22,422	8,102	6.17	225.81	25.72	2.310	44.84	Sludge

BASIS:

- U.S. Environmental Protection Agency data from Report EPA-600/2-75-006
500 mw new coal-fired power unit, 3.5% in fuel; 90% removal; 10.3 tons/hr SO₂.
No credit taken for recovered product.
Stack gas reheat to 79°C (175°F)
Midwest plant location represents project beginning mid 1972, ending mid 1975, average capital cost basis mid 1974.
Minimum in process storage, only pumps spared.
Closed loop water utilization for gas cooling stage.
Investment for disposal of fly ash excluded.
Construction labour shortages with accompanying over time pay incentives not considered.
Operating costs are projected 1975 values.

- Spring Estimates

The design basis selected is 73,000 acfm of gas to process at 400°F at the SO₂ concentrations shown and an SO₂ emission of less than 200 ppm by volume, dry basis. The operating costs include the induced draft gas fan power requirement, gas cooling and all operations through delivery of product SO₂. Fixed charges and capital related costs are excluded.

SO ₂ in gas to process, percent by volume, dry basis	Cost per Short Ton of SO ₂ Recovered		
	0.2	1.0	2.0
SO ₂ Recovered, percent	90	98	99.8
SO ₂ Recovered, Tons per day	10	50	100
Power @ \$0.009 per kwh	\$ 7.34	\$2.13	\$1.36
Steam @ \$2.00 per M lb	16.50	6.52	5.32
Cooling Water @ \$0.02 per M gal	0.10	0.12	0.13
Absorbent Process Losses	1.10	0.55	0.55
TOTAL	\$25.04	\$9.32	\$7.31

The process system is well instrumented to ensure stable operation with minimal labor requirements. It is essentially free of purge streams other than the discharge of the particulate scrubbed from the feed gas. The high concentration of the SO₂ product permits efficient conversion to liquid SO₂, elemental sulfur or sulfuric acid.

Reference 1 EPA-600/2-75-006, January 1975 publication of the Office of Research and Development U.S. Environmental Protection Agency, entitled "Detailed Cost Estimates for Advanced Effluent Desulfurization Processes".

STARTUP OF AMERICAN AIR FILTER'S
SULFUR DIOXIDE REMOVAL SYSTEM AT THE
KENTUCKY UTILITIES COMPANY'S GREEN RIVER STATION

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I. INTRODUCTION

The sulfur dioxide and particulate collection system for generating units #1 and 2, and boilers #1, 2, and 3, (Figure 1), at the Kentucky Utilities Green River Station consists of a tail end lime scrubbing system. A turnkey contract for this project was awarded to American Air Filter in June, 1973, and startup commenced September, 1975. Generating capacity of the combined units is 64 MW, with fuel being primarily high sulfur Western Kentucky coal. The system consists of one scrubber module to handle a maximum of 360,000 ACFM at 300°F. The blow through scrubber module, see photo, contains an adjustable throat flooded approach venturi for flyash removal, a mobile bed contactor for SO₂ removal, and centrifugal demister. Pebble lime storage, slaking facilities, and pumping system provide reagent slurry which is pumped to the three-compartment reactant tank. Bleed slurry from the tank is pumped to a settling pond, and clear water from the pond is to be returned to the system for closed loop operation. This report depicts events through October 9, 1975.

II. SYSTEM DESCRIPTION

The two generating units are used for peak loads; therefore, the boilers supplying steam to the generators are normally run only five days per week, with one or more of the boilers often at reduced capacity. Wide fluctuations in gas flow to the scrubbing system, as well as system shutdown every Friday afternoon and startup every Monday morning, had to be considered in the design.

The flue gas is drawn from the existing breeching through a guillotine type isolation damper and duct system to the scrubber fan. From the outlet of the scrubber fan, the gases flow through a venturi scrubber which was provided primarily to remove the particulate escaping the existing mechanical collectors. The gases then flow upward through the mobile bed contactor, where the slurry reacts with the SO₂. The contactor bed consists of ten separate compartmentalized sections with overhead slurry sprays and below-bed dampers to accommodate gas volume turndown requirements.

The slurry/recycle system, Figure 1, consists of a reactant tank with recycle pumps supplying the contactor and venturi, a lime slurry slaking and feed system, and a bleed system discharging to a large pond with return water from the pond to be used as primary make-up. Spent slurry exits the scrubber into the return section of the reactant tank, where make-up water and fresh reagent are added. The second and third compartments of the tank provide for completion of the chemical reaction. Agitators in all three compartments maintain

solid suspension. Rubber-lined recycle pumps convey the screened water from the third (feed) compartment back to the venturi scrubber and mobile bed contactor.

The lime slaking system consists of a 500-ton capacity pebble lime storage bin which is filled by pneumatically unloading lime received by rail. The lime storage bin has a vibrating bottom and screw feeder, which feed the pebble lime into an agitated slaking tank. From the slaker, slurry is discharged into a large agitated hold. Reactant pumps feed the reactant as approximately 20% slurry to the return section of the reactant tank in response to pH sensing instrumentation.

The bleed pumps remove reaction products and collected flyash from the reactant tank to maintain an approximate 10% slurry within the tanks by pumping slurry to the pond where the solids settle, and clear water is returned from the pond by pumps to the return section of the reactant tank to maintain the proper liquid level.

Treated water (cleaned river water) for make-up is brought into the system through the pump gland seals, the slaking operation and through the demister wash nozzles.

Extensive instrumentation is provided to match gas flow from the boilers by a pressure sensing loop in the ductwork to the main scrubber fan, to control the number of bed dampers that are open, to control the system pH, to control the venturi pressure drop and to monitor other important functions.

It will not be the purpose of this paper to discuss the design considerations of the system nor the chemical aspects of the startup, as these considerations will be covered in a separate paper. It will also not be the object of this paper to discuss the methods of training and operator participation as this is also to be covered in another paper. The primary purpose of this paper is to discuss the philosophy of the startup and some of the problems encountered.

III. PHILOSOPHY AND PLANNING FOR STARTUP

Experience had shown that careful preparation must be made for startup to prevent the chemistry episodes experienced with other SO₂ systems. Hence, startup was to be divided into four phases. The first phase would consist of mechanical and electrical debugging, which would include running the agitators and pumps.

The second phase would include operation of the unit on air and water only. During this operation, various gas and liquid flows, operation of dampers, and spray patterns would be observed and calibration accomplished. During the latter part of the air and water test, the seed crystals would be added so that a slurry could be pumped through the system.

The third phase would be a mechanical proving phase in which the unit would be run on air and water under the control of the operators as a normal system. The purpose of this phase was to catch any early failure in mechanical equipment so that the final flue gas run would not be complicated by such problems.

The fourth phase would consist of operation handling flue gas on a round-the-clock basis for a sufficient length of time to verify that the system would operate satisfactorily before commissioning and final turnover.

To perform the work under these various phases, manpower was to be supplied by AAF, Kentucky Utilities, and their mechanical and electrical contractors. In addition, once the flue gas phase had begun, an analytical team would be employed around the clock from AAF's Research and Development Group to give advance warning of potential chemical scaling.

IV. AIR AND WATER TESTS

Following general electrical and mechanical debugging, startup for the air and water phase began in August. Upon startup of the main fan, stack oscillation occurred. This was not a consistent problem, but appeared to vary in relation to air flow through the system. AAF, utilizing its Pulsco Division, determined that a standing wave was forming within the system that exactly matched the demister and stack natural frequency, causing the oscillation. An anti-spin device was designed and installed within the upper portion of the demister, solving this problem. Also, during this test, minor modifications were made to the cyclonic demister to achieve the required performance. By positioning deflectors and drip rings at carefully analyzed points, mist carryover was eliminated. Concurrently, a careful analysis was made of the mobile bed contactor. Engineering personnel observed spray patterns from within the unit to verify sphere movement through a range of gas flows, and performed other tests. Nozzle locations were optimized, and further nozzle study work was begun.

While this work was being done, a number of the control loops were confirmed or modified. Other minor work, such as installation of additional pipe supports, and access modifications was performed.

Just prior to the completion of the work, the lime bins were charged with pebble lime and the slaker was operated. The slaking equipment operated satisfactorily, although there were initial minor problems with the lime feed system. Bridging would occur across the slake tank, which would then result in cave-in and splashing. The lime feed screw conveyor was simply adjusted to the proper speed, and this problem was eliminated. The mix hold tank was filled approximately half full of 20% lime slurry in preparation for the flue gas run.

V. MECHANICAL RUN

After making the abovementioned adjustments, the system was run continuously for approximately two weeks to uncover any additional mechanical difficulties. Mixer malfunctions occurred, including a motor failure and faulty drive train assembly. Near the end of the two-week run, gypsum seed crystals were added to the reactant tanks, and the system was run for a few days under this condition.

VI. FLUE GAS RUN

The flue gas run commenced the morning of September 13, 1975. Startup occurred and subsequent operation was at 50% capacity as one of the generating units was off line for major repairs. Slurry samples were withdrawn from specified points hourly to monitor pH and per cent solids and to verify sulfate saturation level within the system. The inlet SO₂ analyzer plugged with flyash within a few hours, and has since required frequent calibration and cleaning.

During the first day's operation, bunkers were filled with 1.6 to 2.0% sulfur coal having ash content ranging between 15% and 25%. This low SO₂ concentration and low evaporation rate due to 50% gas flow resulted in a minor water imbalance as water entering the system through pump glands and demister wash was greater than the amount lost through bleed plus evaporation. Solids content in the recycle system increased very slowly because of the low sulfur content and resulting low solids precipitator rate. The unit was shut down for a routine inspection after several hours' operation, no problems were observed, and the system was put back on line.

With one generator down for repairs, it was necessary to begin operation of the I.D. fan for the third boiler at nominal flow, as flue gas leaked from the third boiler breach connection. This resulted in high excess air and low SO₂ inlet concentration. During this fan startup, the system automatically went on bypass proving the duct pressure control loop. Taking

advantage of this bypass, the scrubber fan was shut down and an inspection was made. Additionally, a shield was installed around the SO₂ analyzer inlet probe to prevent it from plugging with flyash. Upon re-start, the SO₂ analyzer indicated approximately 1,200 ppm entering the system, consistent with the level expected from the combination of low sulfur coal and dilution air from the third boiler. Operation during this period was primarily under a manual mode; pH readings were inaccurate due to poor slurry circulation at the probes. The sensing probes had been placed within still wells within the reactant tanks, and although the agitators provided more than adequate movement within the tanks, the still wells employed for probe protection didn't allow adequate slurry circulation and blockage occurred. The probes were then removed from the still wells and installed elsewhere in the tank which provided for adequate circulation and with ultrasonic cleaning resulted in reliable operation. Ultrasonic probe cleaners were further modified at the manufacturer's request to provide better performance. A pH override control was modified to increase its sensitivity to scrubber exit slurry pH, resulting in improved control response.

SO₂ removal efficiency decreased during the week, with inspection revealing that nozzles were plugged with debris that had not been adequately flushed from the system prior to startup. Nozzles were periodically removed, flushed, and re-installed during the flue gas run.

AAF was aware of the scaling that has occurred in other systems and took pains to carefully inspect this system during periodic shutdowns to identify the formation of scale.

Scaling has not been a problem, although some film of scale has been noted. This has tended to disappear with continued operation.

The SO₂ removal efficiency of the system was generally in the mid-nineties range, with a varying inlet concentration of SO₂ as the sulfur in the coal changed.

SUMMARY

The initial phases of the startup of this system have followed a carefully planned procedure. Some mechanical problems have been experienced, but solutions have been found as the problems occurred.

The wide range of sulfur content in the coal burned as well as the high equivalent excess air in the flue gas tested the system's ability to respond to changes.

The SO₂ removal capability and the absence of measurable scale in the system are most encouraging in this startup.

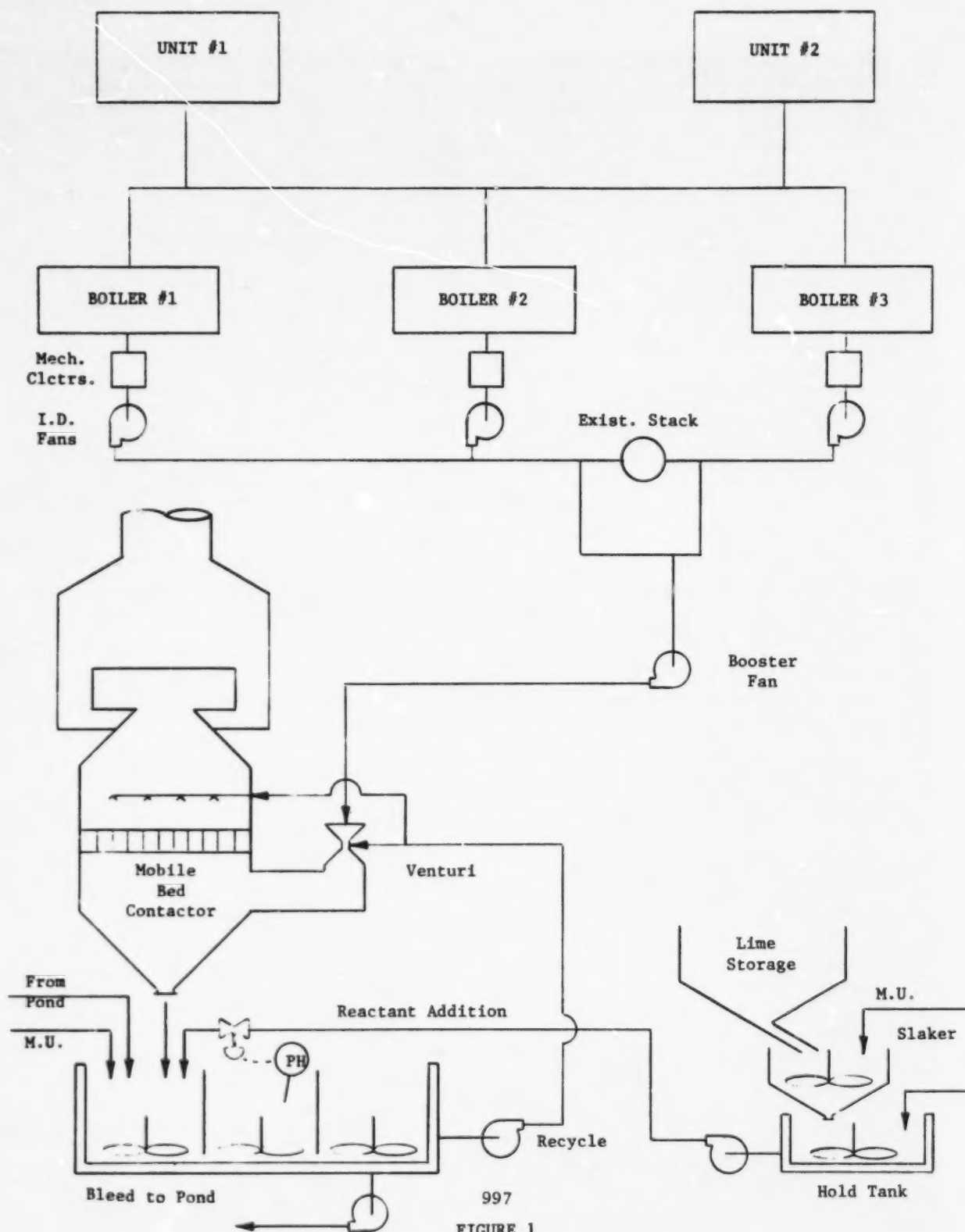
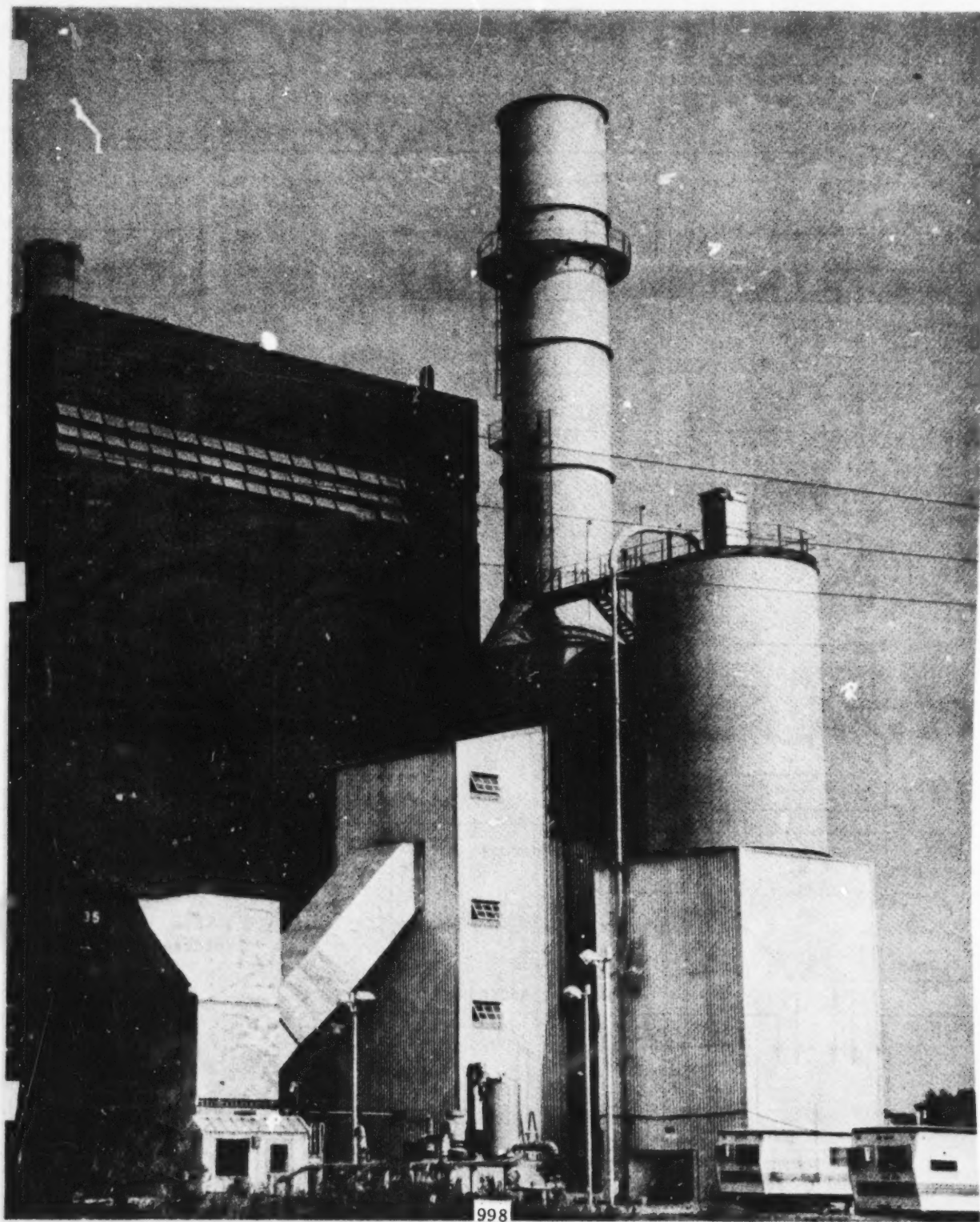


FIGURE 1



TCA SPHERE DEVELOPMENT AND EVALUATION

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ABSTRACT

The requirements for fluidized-bed packing (spheres) have become more stringent as the application of TCA scrubbers has expanded from use in industrial processes to flue gas desulfurization and particulate removal. To meet these requirements a continuing program of sphere improvement has been maintained by the Air Correction Division of UOP. The development of representative screening and evaluation tests is critical to this program since the service life of the spheres is to be a minimum of 1-2 years. It is the intent of this report to describe both the sphere program and the various testing and evaluation procedures used.

Economic and operation specifications have indicated that thermoplastic and elastomeric materials should be emphasized. Presently foam rubber spheres have been developed that exhibit extraordinary resistance to service conditions and thus seem to be the ultimate solution of the sphere question. The comparison of laboratory and field experiences demonstrate the continual improvement of spheres for various TCA applications.

TCA SPHERE DEVELOPMENT AND EVALUATION

THE PROBLEM

The Turbulent Contact Absorber (TCA) utilizes a fluidized bed of low density spheres, Figure 1, to provide a contact surface between the liquid scrubbing medium and the gases to be scrubbed. The first standard to be used was a blow molded polypropylene (PPO) sphere, Figure 2. As long as the TCA was being used for chemical absorption with a minimal amount of particulate the PPO spheres performed satisfactorily. As the market for the TCA developed, a high percentage of the applications was for flue gas scrubbing. The presence of fly ash and the use of lime/limestone slurries in these applications produces a high abrasive environment which significantly reduces sphere service life. Field test reports showed service life to be from 2000-4000 hours whereas acceptable minimum service life for power plant application would be at least one year or over 8000 hours.

In 1972, the Air Correction Division (ACD) initiated a comprehensive development program to analyze the sphere life problem and to develop a sphere of the required quality. Analysis of sphere life indicated that abrasion, impact, and oxidative degradation were pertinent factors in PPO sphere failure. The first step in improving service life was to find a material which could be processed to form the required sphere and would withstand the severe impact and abrasion without degradation. The second and more difficult step was the development of a test procedure to justify the material selection and fabrication technique. This accelerated test should help to predict sphere service life without waiting a year for field data. Only with continual progress on the second step could the results of the first be fully realized. In completing evaluation, it is necessary to show that the test procedures are relevant to field service. It will be shown how improvement in technique, and confidence in test techniques has lead to a closed cell foam rubber sphere which meets the requirements for scrubber service.

THE PRODUCT

The sphere under study is 3.8 cm (1.5 inches) in diameter and weighs approximately 5.5 grams. During the development program the design weight has steadily increased from 4.5 grams to the present 6.5 grams. This change has been made by the requirements of scrubber performance. Except for correcting data for different weights, the changes in

weight have not influenced the program. For the best combination of integral strength and production economy, blow molding was chosen. In the blow molding process, a tube of appropriate size is extruded and located between mold halves. One end of the extrusion is clamped shut and the tube is inflated from the other end. The molds close forcing the material into a spherical shell and cutting away all excess material. Five spheres can be blown from each extrusion. During the blowing and molding process a new extrusion is started so that the cycle may be repeated following the stripping of the spheres and waste from the mold. While the process is simple the entire cycle requires the closest control. The quality of the weld seam alone is highly dependent on the strict control of process parameters.

DEVELOPMENT AND EVALUATION

Embrittlement

The earliest serious problem with TCA spheres was embrittlement. The PPO spheres would crack away from the poles towards the weld seam after several hundred hours. Failure rendered the spheres useless long before the anticipated life to the sphere due to abrasion. The mechanism of failure was established as brittle fracture due to impact. This embrittlement was caused by oxidation, accelerated by elevated temperatures. The mechanism was considered inherent to the PPO polymer, so a comprehensive material survey was initiated to find an acceptable substitute and if possible improve the service life of TCA spheres.

The survey resulted in a substitution of high density polyethylene (HDPE) for PPO and the development of thermoplastic rubber (TPR) spheres. The embrittlement and loss of impact strength was determined with the Gardner Impact Test. The same test on HDPE indicated an obvious solution to the problem. This was further verified in field tests and actual service. HDPE spheres have served to the full expected life in abrasive systems with no evidence of brittle fracture. Brittle fracture was the first and simplest problem to overcome.

Abrasion

Of the three factors contributing to sphere failure abrasion has been the most difficult to evaluate. There are many types of abrasion tests; some are designed to simulate specific field conditions and others to measure abrasion resistance in a laboratory. At the outset of the program it was realized that methods must be developed to permit specification of material for abrasion

resistance and to project service life for sample spheres. Abrasion studies developed along the following areas: first, a method to screen sphere materials; second, an accelerated lab test to evaluate sample spheres and finally, service life data to verify accelerated tests.

A wet abrasive high velocity slurry spray was used to screen a large variety of materials. Forty-five different thermoplastic and elastomeric materials were tested in this manner. The results were erratic. However, by assigning fixed values to the control samples it was feasible to assign a relative abrasion resistance ranking. The difficulty of testing and the limited value of the results discouraged use of this technique.

The first attempt at accelerated sphere testing was made with a modified Taylor Ro-Top shaking machine (Figure 3). The specially designed shaker pans were loaded with 30 spheres and a 15% slurry silicon carbide grinding powder. The vibrating action in the closed container with an abrasive slurry simulated sphere to sphere, sphere to slurry and sphere to structure contact. Tests were run during the course of each working day until significant weight loss was recorded. Actual running time varied from 100 to 400 hours. Tests with original polypropylene spheres showed a 17% weight loss per 100 hours of shaker testing.

When compared to results from the pilot scrubber described below, the PPO spheres exhibited a tenfold acceleration for several different tests. Weight losses of 17% per 100 hours in the shaker were equal to 17% per 1000 hours in the pilot scrubber. The weight loss experienced by the HDPE spheres in the shaker was 5% per 100 hours as compared to 11% per 1000 hours for the pilot test. Thus it was realized that there was no simple correlation between the shaker and field test results.

At this point results of the wet abrasive spray tests indicated that TPR would offer a tenfold improvement over the abrasion resistance of either PPO or HDPE. This would almost negate the acceleration factor offered by the shaker test. The shaker test was therefore no longer useful.

Concurrently with the beginning of the above program a 3 stage pilot TCA scrubber became available for sphere evaluation. The unit used ambient air and a counter current flow of a 10% slurry of fly ash that was continually recirculated. The pilot data mentioned above was generated with this system. The TPR sphere tests were run at scrubber operating temperatures. The duct work

was modified and insulated so that the gases would recirculate. Heating elements were installed such that the spheres were in contact with 49°C recycled liquor. It was felt that operation at this temperature would give a reasonable simulation of actual field conditions.

Tests were started immediately to obtain abrasion data for both TPR and HDPE for 7000 service hours. Figure 4 shows the results of these tests. A realistic means of studying abrasion was therefore available, although not on an accelerated basis. Samples were taken from the pilot scrubber after 950 and 5500 hours, subjected to microscopic examination and compared to virgin samples. Included were spheres made of Ethylene-Ethyl Acrylate (EEA) which, while not acceptable, were tested to extend the range of correlation. Both optical and scanning electron microscopy were used. A mechanism for abrasive wear was then projected. On hard surfaces such as HDPE and PPO the particulate is partially imbedded on the surface of the sphere. Subsequent action tears the particulate out along with some material. This process continues with gradual loss of weight. In addition, the protruding particulate acts as an abrasive against other spheres. The TPR spheres on the other hand are elastomeric and therefore have a softer surface. Particulate becomes completely imbedded in the surface. The sphere does not, therefore, have an abrasive surface when contacting other spheres, nor is material lost due to particulate breaking away from the surface. The curves in Figure 4 strengthen this theory. The HDPE spheres are subjected to a nearly constant rate of weight loss. TPR spheres lose some weight initially but between 500 and 2000 hours they appear to gain weight and thereafter the overall weight loss is negligible. It is projected that the weight gain is caused by the assimilation of the particulates imbedded in the surface.

The understanding of a mechanism for sphere abrasion led to accelerated tests. Three methods were tested: sand blasting, pin and disc abrasion and planetary ball mill. In all three methods the mechanism of abrasion was similar to that experienced in the scrubber. In the sand blasting and pin and disc tests the quantitative results could not be easily correlated with scrubber data.

The planetary ball mill approach was more successful. Following the test, the samples are examined microscopically to verify the mechanism of abrasion. Tests on four samples for which scrubber data was available showed a direct correlation, Figure 5. This test has now become an important tool in sphere development.

The present understanding of the mechanism of abrasion has taken

three years to develop. With the constant cross-reference of test results it has been possible to develop test techniques which can be used to evaluate the ability of a sphere to withstand abrasion.

Impact and Seam Strength

The effect of impact on sphere service life has been misleading. The obvious modes of failure in PPO were abrasion and brittle fracture. While impact accelerates brittle fracture, eliminating oxidation embrittlement by the choice of HDPE and TPR as sphere materials solved this problem. In the first field tests of TPR a serious problem with weld line failure was encountered. This led to a comprehensive study of the effects of impact on blow molded spheres. The results of the study have resulted in successive improvements in the quality of TCA spheres.

Initial results in TPR from the pilot scrubber reported 0.4% of the samples failed near the seam. The seam failure was attributed to manufacturing difficulties which should be corrected before production began. The first production lot was sent out to field test based on the pilot experience. Within several hundred hours of operation, large percentages of spheres failed by splitting in half along the weld line. Examination of spheres showed that static loading or single impact would not cause failure. Since TPR is elastomeric, the surface is flexible. Repeated flexure along the weld seam could cause failure. Subsequent investigations showed that material around the weld seam was significantly weaker than the rest of the shell.

Work to strengthen the seam was started immediately by the blow molders with the cooperation of the resin supplier. At the same time a program to quantify seam strength was initiated. The first tests were to repeatedly compress spheres to approximately one half of their diameter. The number of cycles until failure would then indicate the seam resistance to failure. In the test fixtures, spheres were free to rotate so that the axis of compression was random. Post test examination revealed that failure always started on the seam at location shown as "E" in Figure 2.

Results with this approach showed that the cycle life was also dependent on the initial sphere weight. Sphere weight is a direct relation to wall thickness and thus shell strength. Therefore, in an attempt to equalize flexural stress between spheres of different weights it was decided to adjust the amount of compression to be equal to the compression caused by a force of 25 pounds. With this

method, samples from the field test batch averaged 10,560 cycles to failure with approximately 20% of the samples below 1,000 cycles.

The results gave a qualitative relation to the field test i.e., high initial rate of failure with a long service life for the remaining. One further refinement was added. The temperature at which the tests were conducted was raised from ambient to 49°C. Improvements in seam strength were verified using the above technique. Figure 6 shows an example of the progress that was made. The improvements were a direct result of changes in the manufacturing techniques and processing parameters.

At about the same time the tests were being run, pilot scrubber results and field tests showed that HDPE was also subject to seam failure. Since HDPE is a rigid shell, the techniques of the flexure test were not applicable. It was thought that the mode of failure for both types of spheres was repeated impact.

An alternate test method was required. A machine called the "Frag Tester" was adaptable to sphere testing. The Frag Tester is a machine designed to measure the tear strength of paper. With a few modifications, the machine was adapted to measure the seam strength of spheres. In this machine a weighted arm is raised to a preset height and dropped on the sphere under test. The action is repeated until there is a break in the seam. The number of drops to failure is an indication of seam strength.

Unlike the flexure test, the impacts are repeated at a single point. It was necessary to establish the point for consistent testing. The flexure tests showed the "E" point of failure for TPR. This was verified with the Frag Tester, by testing at 12 locations around the seam. It was determined that the lowest cycles to failure occurred at the "E" point. The focus for impact testing was established at that location. Figure 7 shows the correlation between Frag and Flex Test for various production batches of TPR spheres. Each point represents the average cycles to failure of 20 samples, 10 for flexure testing and 10 for Frag testing.

With the help of the Frag tester and the cooperation of the blow molders it was determined that seam strength is a direct result of process parameters. In both HDPE and TPR, the molding cycle and process temperatures are critical. In order to insure acceptable quality, Frag type tests have been installed at the blow molders and have become a regular part of their quality control program. In addition, the molders are required to submit samples to ACD for quality audits.

Dimpling

The phenomena referred to as "dimpling" is common to all flexible or elastomeric spheres. It appeared in the first TPR field test. At that time it was attributed along with splitting, to incorrect material processing. After some careful thought and related tests, the simple explanation became evident: most plastics are porous to gases. Following the thermodynamic history of a sphere will illustrate how the porosity results in dimpling.

After the sphere has been molded and cooled to ambient temperature the gas inside the sphere is approximately at 21°C with a pressure of about 760mmHg and has a relative humidity (R.H.) of say 50%. In a scrubber the spheres are operating at approximately 54°C and 99% R.H. The air inside the sphere has increased in pressure to 863mmHg and the R.H. has dropped to 9%. The porosity of the material permits air to migrate out and water vapor to be absorbed. This may take 100,500 or even 1000 hours. In any case, the migration will continue until equilibrium is reached i.e., the inside gases are at 54°C, 760mmHg and 99% R.H. At this condition, the partial pressure of water vapor is 117mmHg and the air is at 645mmHg. When the scrubber is shut down for any reason the first effect is to react to temperature.

The air will loose pressure according to the ratio of absolute temperatures. The water vapor will condense with a further reduction in pressure. The resulting partial pressure of the air would be 580mmHg and the partial pressure of water vapor is only 18.6mmHg. There is then approximately 160mmHg negative pressure in the sphere. If the shell is not rigid enough to withstand this differential, the sphere can collapse. The mechanism occurs in all spheres, rigid shells will not collapse and while the more flexible TPR do not generally collapse, whenever subjected to outside loading they will collapse or "dimple".

To overcome dimpling it would seem logical to either impart abrasion resistance to a rigid shell or impart rigidity to an abrasion resistant shell. Attempts to find an abrasive resistant rigid shell have been fruitless. Blending HDPE or PPO resins with TPR to increase rigidity have always been accompanied with losses in abrasion resistance.

Field Reports

Of necessity the validity of laboratory procedures has rested heavily on comparison with results obtained from the pilot scrubber. It has been possible to gather some field data for comparison with the pilot scrubber. Figure 8 shows the latest available data from scrubbers operating on line. The correlation between field and pilot scrubbers for particulate removal is excellent and is the basis for accepting all current test procedures. As might be expected, the wear rates for lime/limestone slurries are higher in both HDPE and TPR.

Seam splitting in the field has been harder to correlate. Because of the tedious labor involved in counting failures, field reports have been a simple statement as negligible, minor or unacceptable. It has been possible to determine that spheres which last more than 100 Frag cycles will not split in scrubber service. The difficulty in reducing seam failure is inherent in that seam strength can only be monitored by destructive testing. With the use of appropriate statistical techniques the rate of failure has been held to less than 0.5 percent. Unfortunately the results of seam failure even at 0.5% are particularly troublesome when accumulated in the scrubber sump.

The occurrence of dimpling in the field is an accepted fact. The percentage of dimpled spheres increases with each shut down. On the basis of present reports, scrubber operators have accepted dimpling of TPR spheres in lieu of weight loss and splitting in HDPE. ACD however has not accepted dimpling and has continued to seek a solution to the problem.

CLOSED CELL FOAM RUBBER SPHERES

The entire sphere development program led ACD to a design paradox. In using an elastomeric material which does not abrade, a flexible shell results which dimples. If the shell is made rigid, the abrasion resistance is significantly reduced. The cause of both problems is in the basic function of the TCA and therefore cannot be altered. Because of the low density of the spheres, 0.16-0.24gm/cc, homogenous materials are not applicable. The next approach then was to use some form of a foamed material.

The first step was to select a material which could be foamed, would have a solid skin and have the various other properties which are required for service in a scrubber. The material would have to be elastomeric so as to be abrasion resistant, at least as well as TPR. Two categories were considered, the urethanes and rubber. Generally urethanes have not been considered as suitable materials for TCA service due to their acid sensitivity. Although recent developments are overcoming this problem, it was decided to delay investigations of urethanes in favor of rubber.

The selection of a suitable rubber compound was simplified by the existing list of compounds already screened as serviceable for scrubbers. With the help of manufacturers representatives, it was possible to select a rubber compound which would have the required specifications and could be processed to obtain the sphere of the right density. The material chosen was a modified polyvinyl chloride-nitrile rubber. It is both acid and alkali resistant, abrasion resistant and flame retardant. It is readily blown to form a closed cell foam of the required density and has a solid skin. Feasibility was shown with spheres formed in a single cavity transfer mold. Various formulations were tried until an appropriate stock recipe was obtained. The recipe was transferred to a qualified rubber processor for development. The first samples were received from the processor in December, 1974, and the process of evaluation began. Before the end of 1975, almost 2000 spheres had been received and subjected to the various testing programs. By June, 1975 test results were so encouraging that an order was placed for production tooling. By the end of 1975 production had started and the first placement of foam rubber spheres for field test was made.

Although the material was specified for adequate chemical resistance sample spheres were subjected to routine chemical tests as verification. Similarly, tests were run for flame retardance. The spheres were more than adequate on all points. Although there is no seam in this type of sphere, the samples were subjected to the Frag test to note their reaction to impact. These preliminary tests provided confidence that the spheres would withstand the environment in the TCA. A representative sample was placed in the pilot scrubber for simulation of service life as it was necessary to determine if there was a mode of failure which had not been anticipated.

The results of the pilot scrubber were encouraging. In over 4000 hours of operation there were no incidents of sphere failure.

No significant change was noted in shape and skin texture. No splits, cuts or other flaws were noted. There was definite evidence of water absorption. Weights increased gradually until equilibrium was reached at approximately 125% of the original weight. Water absorption was verified by placing the spheres in a warm dry atmosphere for several hours. In that time, spheres would return to within 1/2% of their original weight. Figure 9 is a graph of the change in weight in comparison with HDPE and TPR.

The results of the accelerated wear tests were fortunately independent of absorption. The tests are run in one hour increments for a total of 5 hours. At each increment the samples are dried and weighed. Since it takes over 1000 hours to reach absorption equilibrium, the effect as compared to the abrasion loss is negligible. The drying also minimizes any effect. The weight actually lost in 5 hours is 0.135% of original weight as compared to 0.16% for TPR. On this basis, the estimated time to wear through the skin of the foamed ball is 12,000 hours.

Since no failures were established in the pilot scrubber, the accelerated wear tests were run past the 5 hours until surface flaws occurred which penetrated the skin of the sphere. At this point numerous craters and splits were produced which exposed the internal cells. It was of particular interest to determine if the exposure of the inner cells affected the rate of absorption. The scarred samples were soaked in water with several new samples as a control. Almost identical weight gains were observed, thus when the skin is abraded or otherwise damaged, no appreciable change in the action of the mobile bed is expected.

In the earlier discussion of dimpling, it was shown that the mechanism is a function of gases trapped in a shell of elastomeric material. In the foam rubber sphere, the single gas cavity has been replaced by millions of tiny cells separated by a lattice of rubber. The mechanism of dimpling also occurs in these cells but does not result in an appreciable change in shape or usefullness. In the newly made condition each of the cells is pressurized. This places the skin in tension holding the diameter. During service the pressure is relieved through diffusion and the gases in the cells reach an equilibrium in both pressure and humidity at operating temperatures. When the spheres are returned to ambient temperature, the internal pressure becomes less than ambient and the skin goes from a state of tension to one of compression. Since the sphere is made of an elastomeric material this change will result in a dimensional change. The phenomena is witnessed when cutting samples in half. When split, a new sphere will bulge out in the center

such that the two halves can not be reassembled surface to surface. In splitting a sphere which has been in service long enough for equilibrium to be reached, the cut surfaces do not bulge and may be placed together in surface to surface contact. Thus it has been shown that the mechanism of dimpling has occurred but because of the change in structure, the results cause no change in the effectiveness of the spheres as a mobile bed.

CONCLUSION

In the continuing effort to improve the quality and service life of TCA spheres, ACD has been able to reduce the severe environment of the scrubber to laboratory test procedures and life tests. Realizing that a commercial TCA installation requires anywhere from 750,000 to 1,500,000 spheres for operation, the importance for sound laboratory procedures is easily understood. Fortunately, through the cooperation of several customers and test facilities, it has been possible to correlate the results of the laboratory with field data. Over the course of the program the solution to each problem has been closely followed by the challenge to extend the service life still further. No sooner had HDPE been substituted for PPO and the brittle fracture problem solved, then the challenge to extend the life due to abrasion from 4000 hours to 8000 hours was made. In the development of the TPR sphere the promise of 8000 hours life was a reality. This was followed by the problems in manufacture which resulted in weld seam failure. With the cooperation of the blow molders this problem was finally overcome after lengthy and difficult experimental programs. With the solution of the seam problem came the realization that dimpling in TPR spheres was a bothersome problem that would not be long tolerated. Finally as a result of all of the technology acquired over the duration of the program, an approach was conceived and developed which adequately meets the rigid specifications for TCA scrubbing spheres. The foam rubber sphere has been and will continue to be evaluated and tested against standards which were not envisioned when the first PPO spheres were ordered for TCA service.

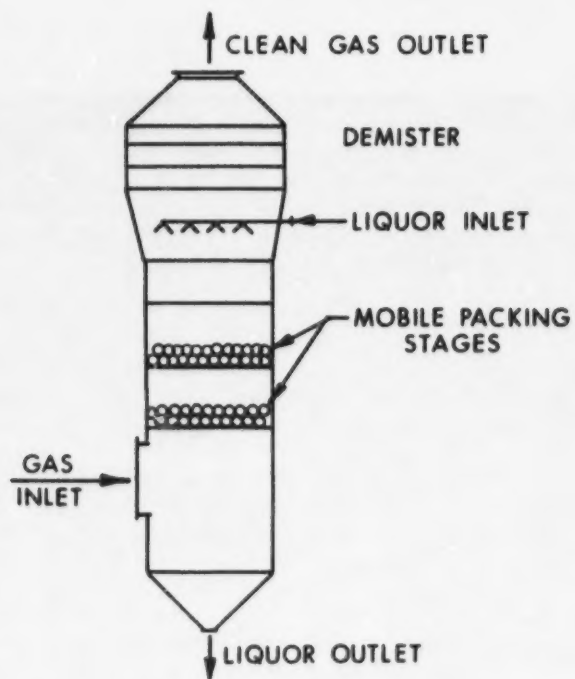


FIGURE 1 TURBULENT CONTACT ABSORBER

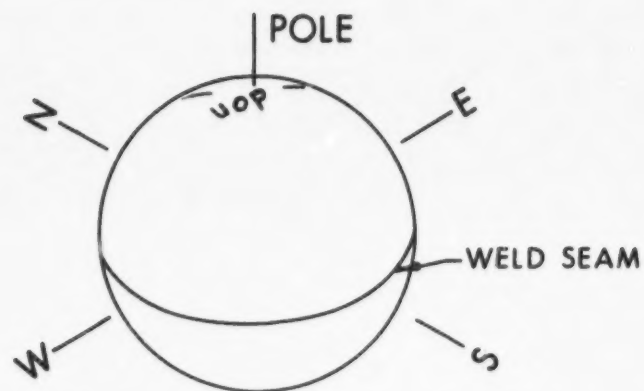


FIGURE 2 MOBILE PACKING SPHERE

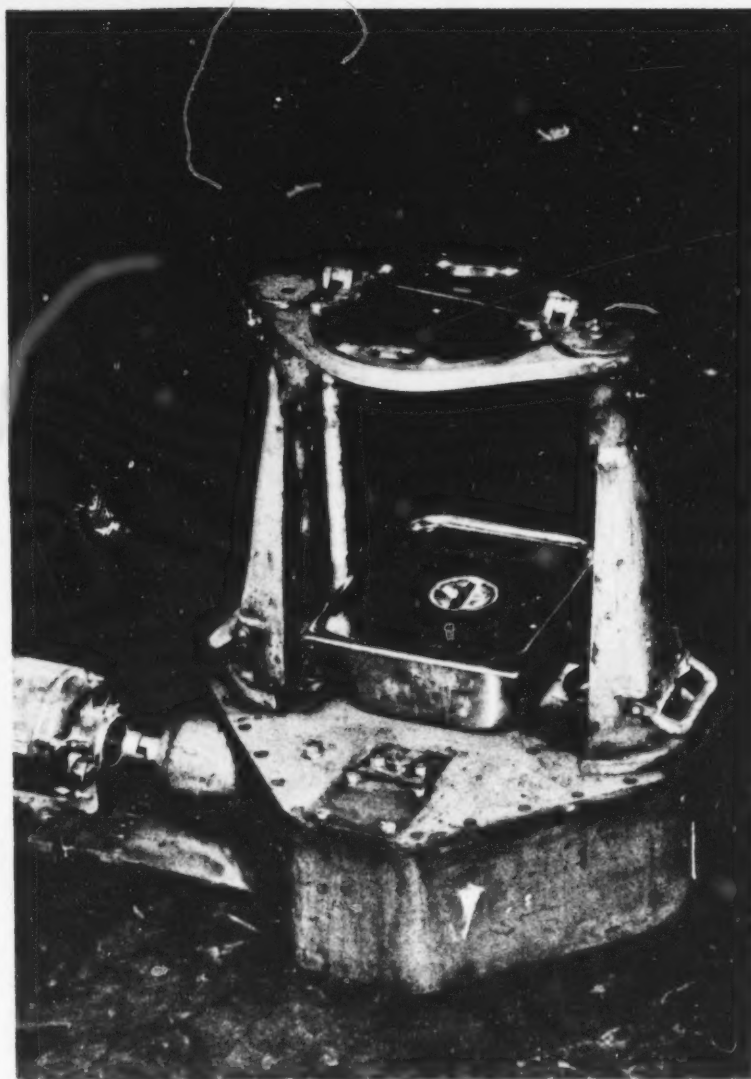


FIGURE 3 TAYLOR RO-TOP SHAKER

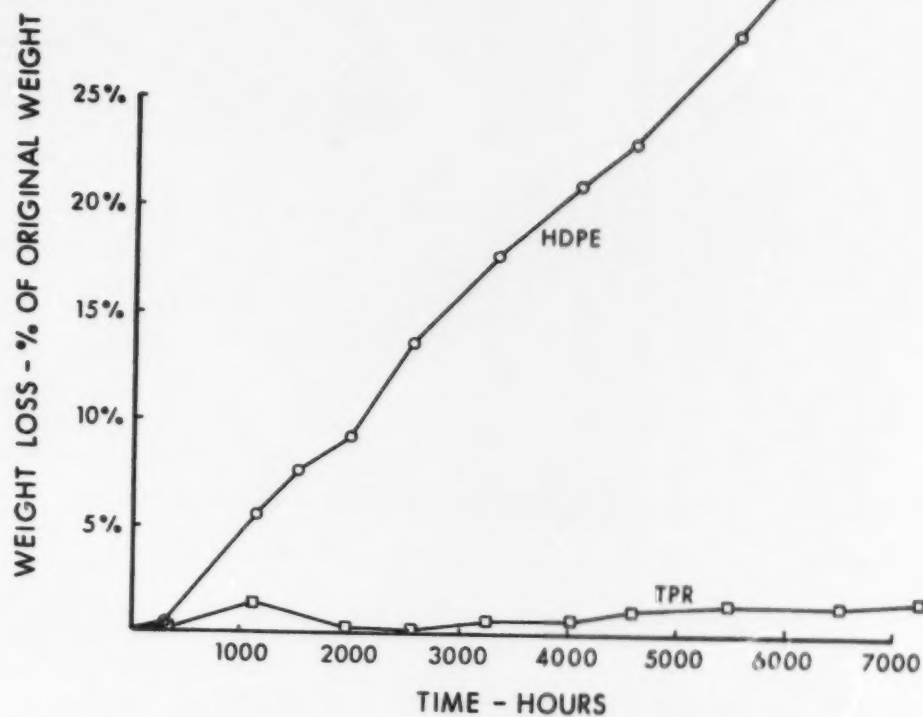


FIGURE 4 WEAR RATE PILOT SCRUBBER

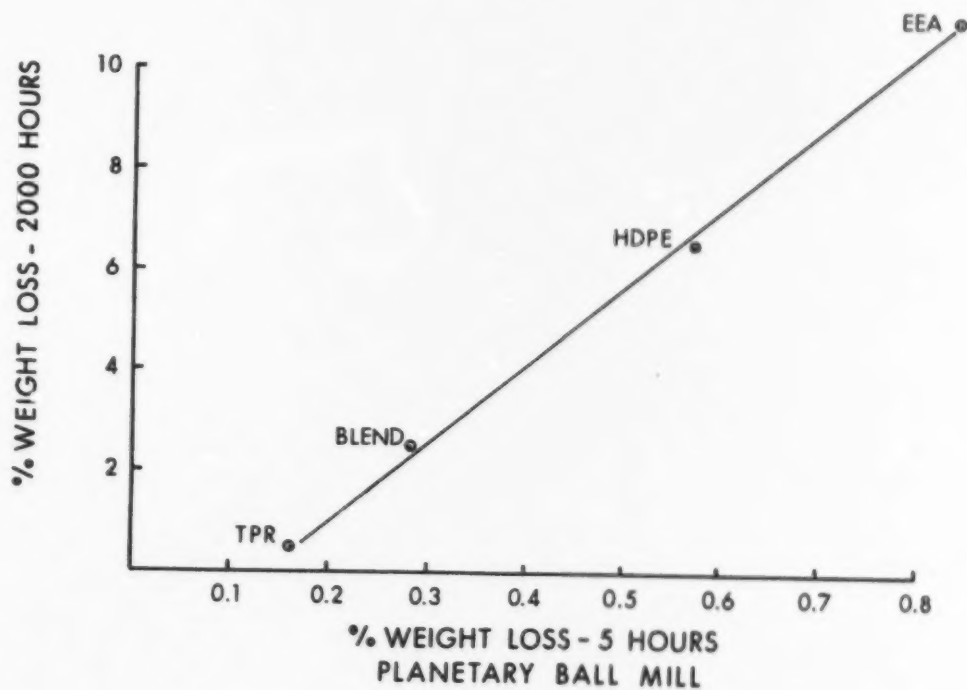


FIGURE 5 WEIGHT LOSS CORRELATION

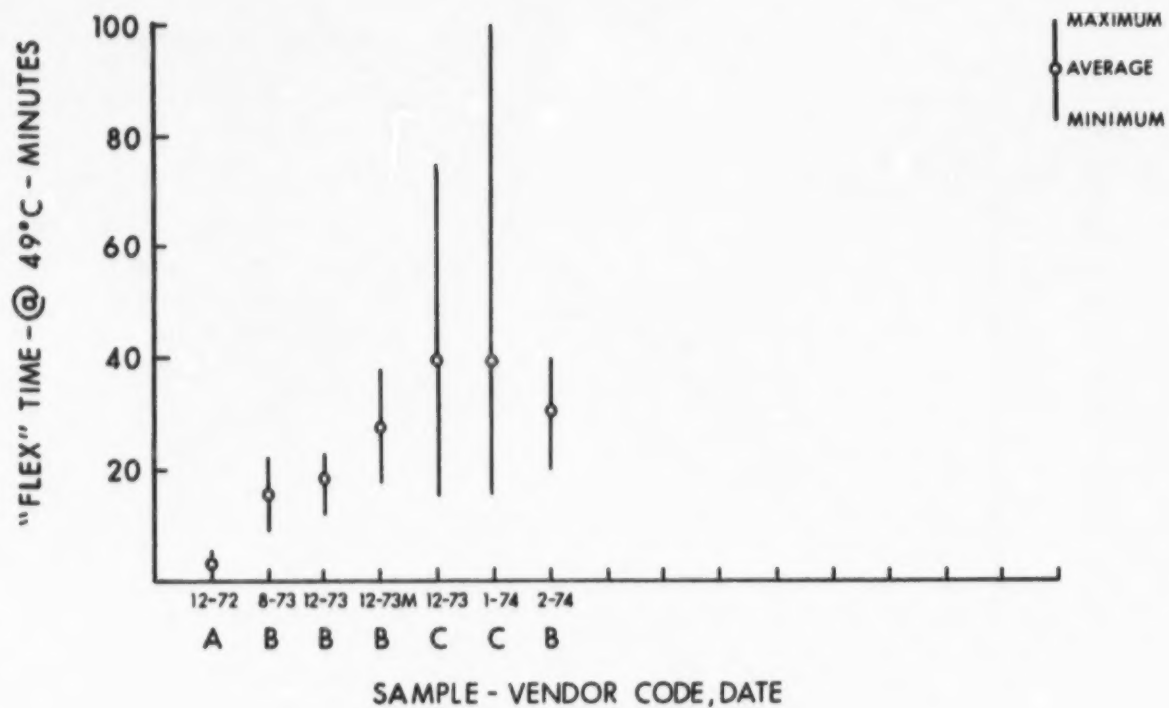


FIGURE 6 SEAM STRENGTH FLEX TESTS

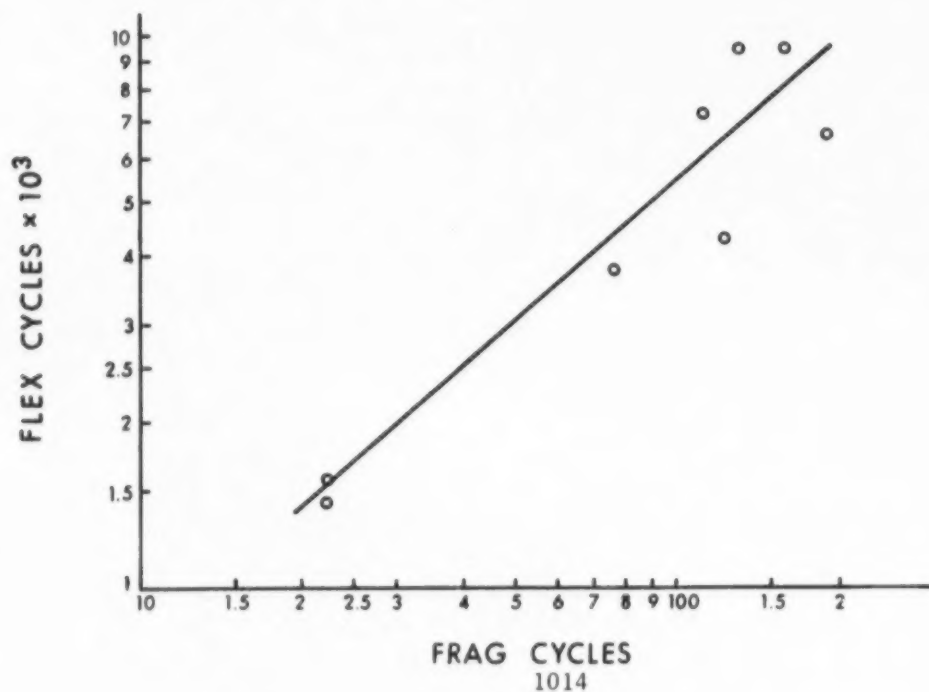


FIGURE 7 IMPACT TEST CORRELATION

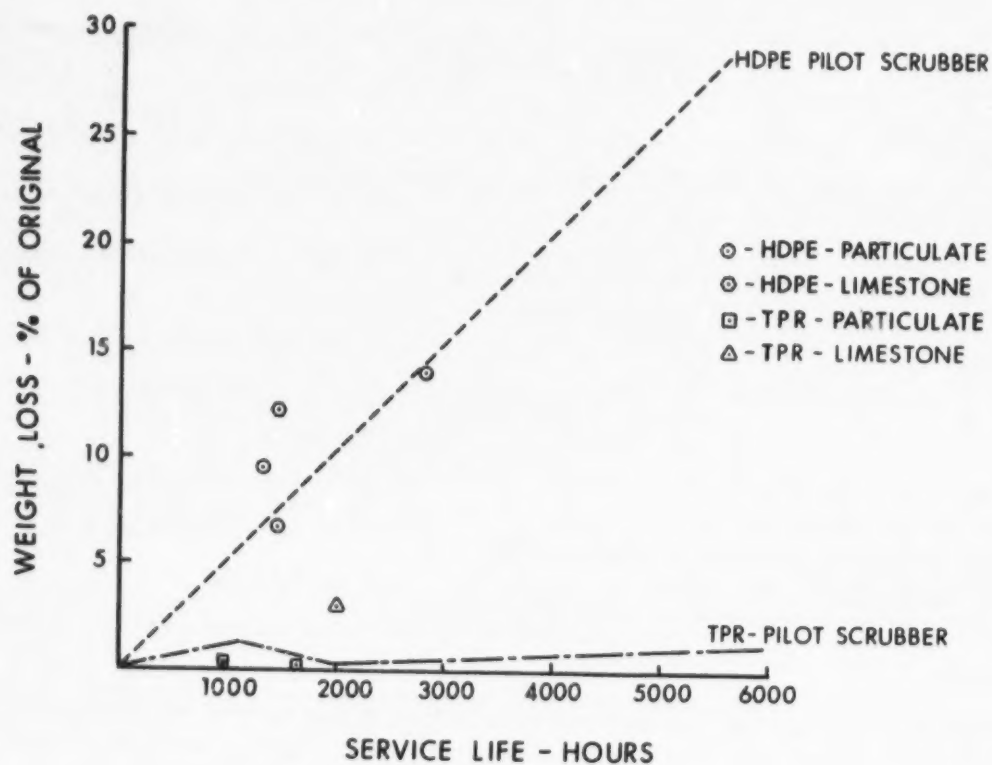


FIGURE 8 FIELD SERVICE - ABRASION

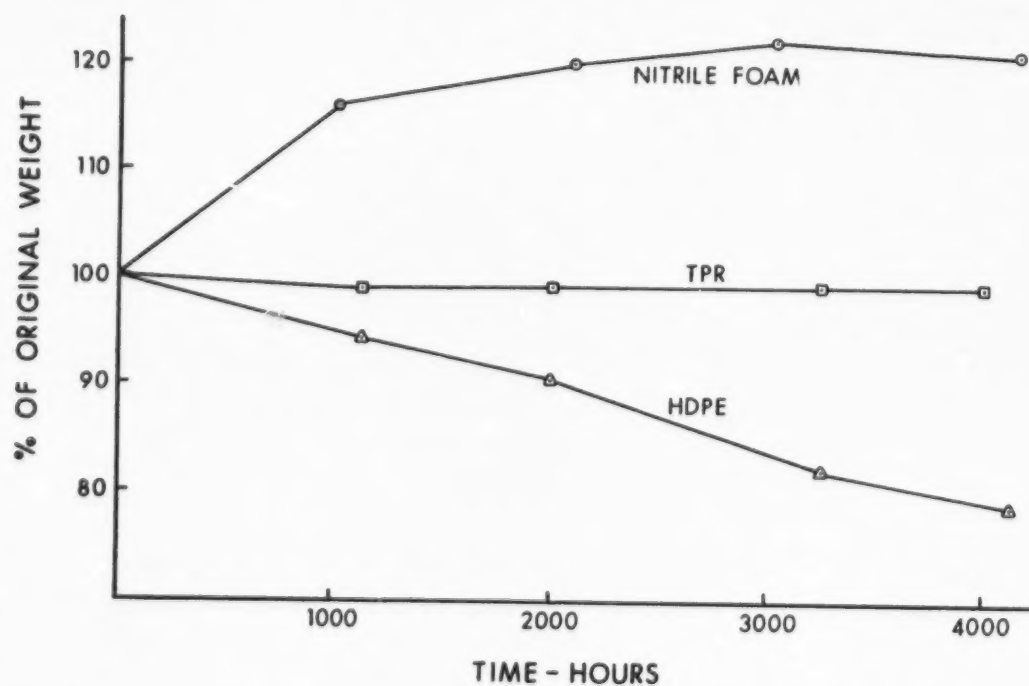


FIGURE 9 WEIGHT CHANGE IN PILOT SCRUBBER